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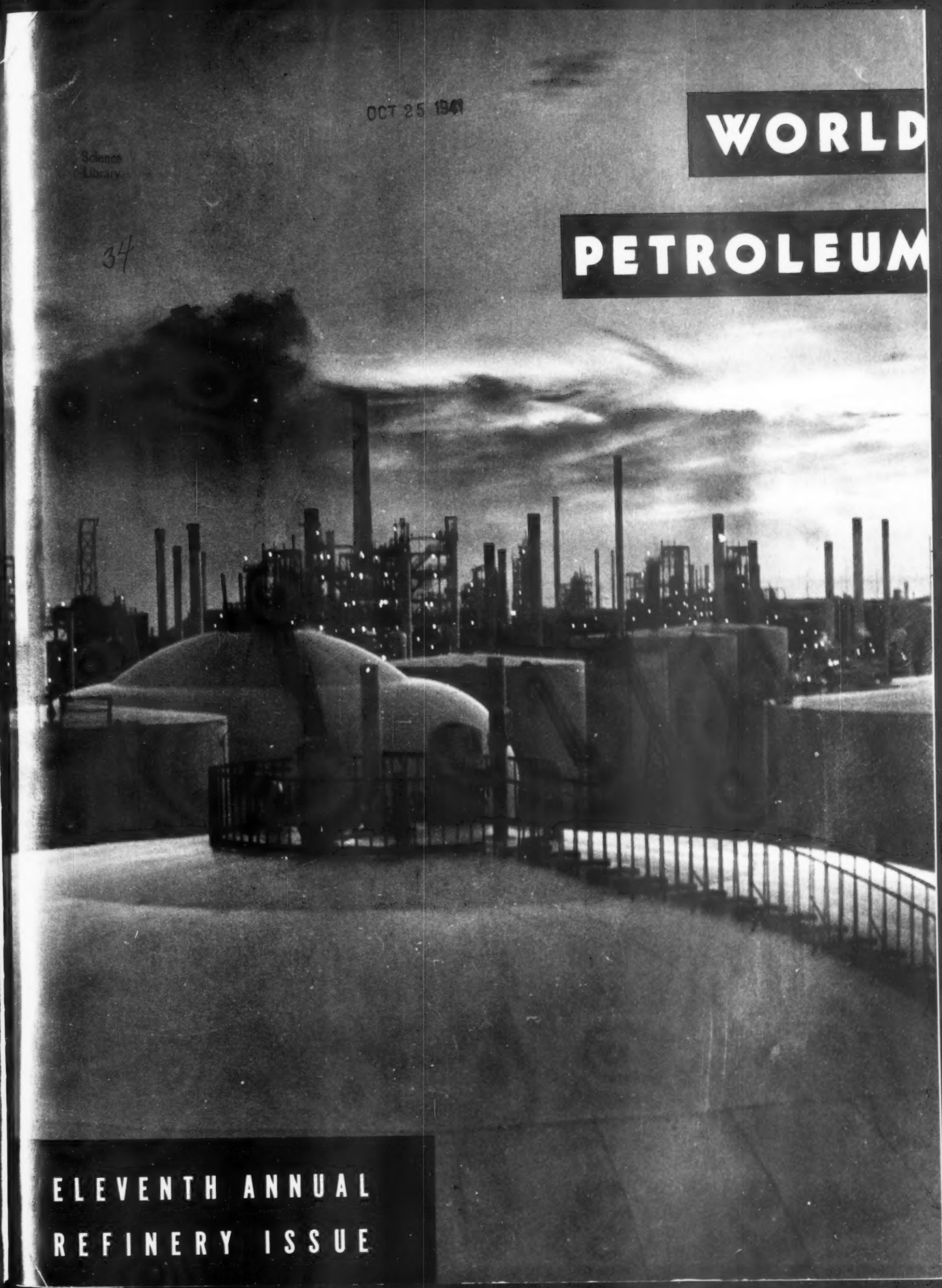

ELEVENTH ANNUAL
REFINERY ISSUE

...— V for U.S.A.

America

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WITH the automobile came the American-Way of Life, that has made the United States the greatest industrial nation on the face of the globe, with over 6,000,000 men and women earning their living in the Petroleum and Automobile Industry. Today all these resources of a great peace time civilization are available for a new era of defense that is the hope of the world's democracies. From a few barrels capacity of the first Hanlon plant built in 1908 that was the beginning of a new Industry—Natural Gasoline, Hanlon-Buchanan now supplies domestic, coastwise and foreign markets daily with thousands of barrels of uniform Stabilized Natural Gasoline—STA-VOL-ENE the "Natural" known throughout the World.

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Incorporating Petroleum Equipment Exporter

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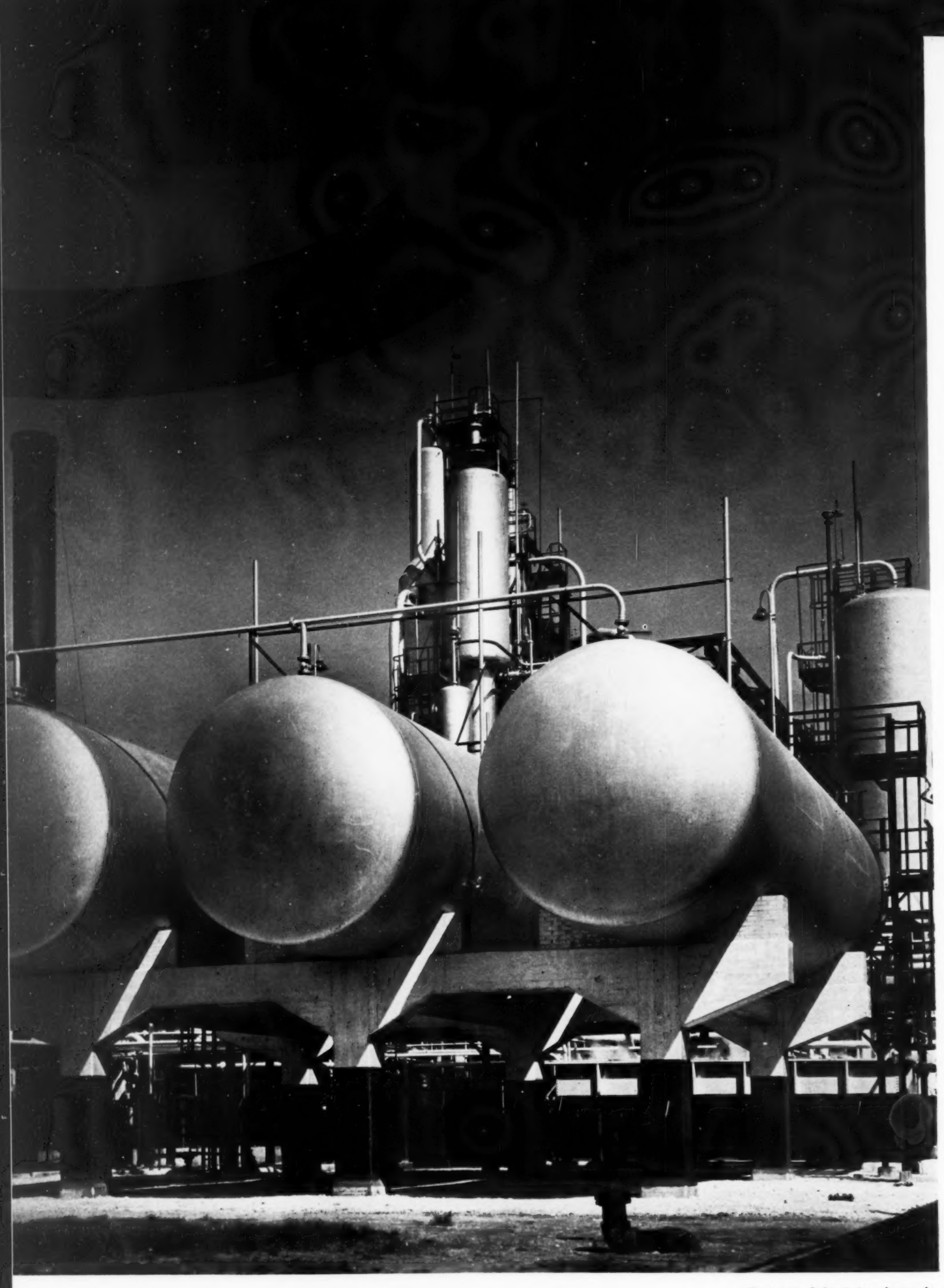


Front cover & frontispiece photographs
by Robert Yarnall Richie

EDITORIAL

REFINING INDUSTRY FACES GREAT WAR AID TASK

Today the American refining industry faces a situation unique in its experience. It is being asked to put itself on a war footing because of a war in which the United States is not a participant but in which it is virtually the only source from which the opponents of totalitarianism can obtain the materials requisite for victory. In the first world war the oil industry contributed importantly, perhaps decisively, to the success of the Allies. But that was when the mechanization of human conflict was in its infancy. Armies still traveled on their feet; artillery was moved by animal power; the tank was a novel but unproved weapon and the few airplanes in service played a spectacular but unimportant part in the struggle. Oil gave a new efficiency to naval vessels; it rendered a useful service in the movement of motor cars and trucks, but it had not reached the position of being the indispensable requirement of every large scale military manoeuvre.

It is not necessary to go into great detail to show how profoundly conditions have changed. Guns, troops and supplies are moved by liquid fuel on land as well as on the sea. Tanks have become traveling fortresses, the most formidable weapons of mass attack yet developed. Above all else the transfer of combat to the air, with huge fleets of fighters, bombers and other types of planes carrying death and destruction hundreds of miles behind the fronts to which fighting formerly was confined, has made oil a supreme factor in modern conflict. Experience of the past two years has shown that it is no longer the heaviest battalions but the swiftest and most powerful airplanes that assure safety in defense and supremacy in attack. It is hardly an overstatement to say that if all petroleum supplies were suddenly to be withdrawn the war would come to an end because the armies would be rendered immobile.

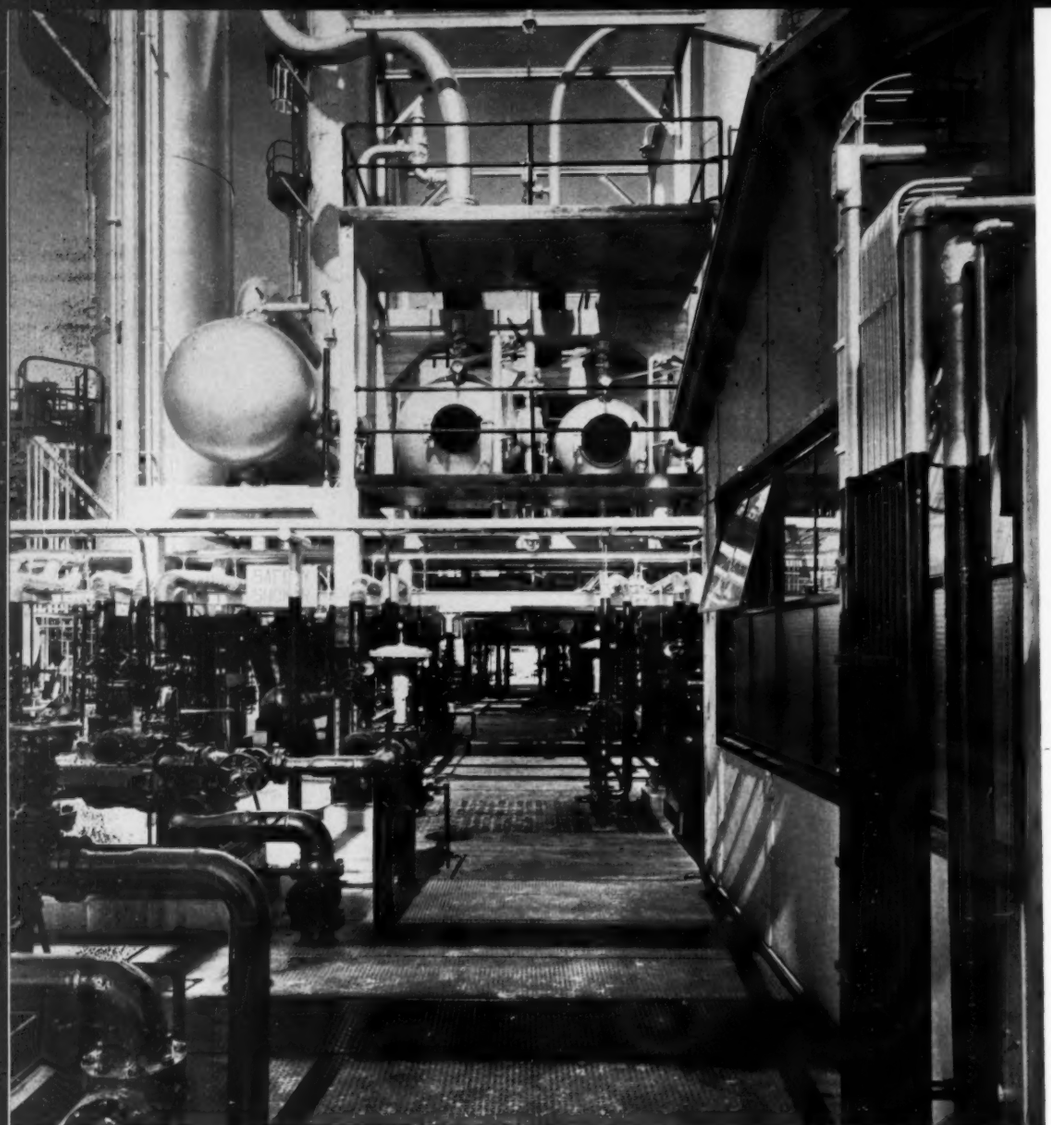
Twelve months ago the refining industry was moving forward to fulfil its part in a purely defensive program designed to make the nation secure against attack by augmenting its army, doubling its naval strength and vastly increasing its air force. It had been asked to increase its output of aviation gasoline by 100 percent and was well on its way to accomplishing this result. To meet the demands of the preparedness campaign in other respects the industry had only to expand its normal operations to an extent which at most was estimated at not more than ten percent.

Since then great changes have taken place both in the scope and reach of the war itself and in the national policy regarding it. Under its greatly expanded armament program in addition to the lease-lend law and the decision to extend all possible assistance to those nations fighting to defend what are conceived to be the interests of the United States the demands upon the oil industry have been vastly increased. A measure of the change is to be seen in the fact that Britain and the Soviet Union alone are calling for as much aviation fuel as the entire quantity calculated as sufficient for all requirements in the earlier stages of defense planning.

Revised plans dictated by recent developments and anticipated necessities now look to a trebling of current production of 100 octane number gasoline, the touchstone of successful aerial warfare, a big boost in the output of toluene, butadiene and its resultant product, synthetic rubber, more solvent lubricating oil units and a general expansion of refining capacity. It is a stiff order calling for high engineering skill and the investment of hundreds of millions but the oil companies and the suppliers of refining equipment are prepared to fill it, provided only that the materials needed for plant construction and operation are obtainable. In a race against time this is the paramount consideration.

Fortunately the oil industry has been in training for a long time to meet exactly such an emergency as has now arisen. In the all-important matter of iso-octane production the millions of dollars expended yearly in research has resulted in the development of processes which make possible an expansion of output limited only by the supply of materials permitted by the demands of other refining operations. Utilization of gases formerly wasted, development of catalytic methods permitting the recovery of high grade products from low grade materials, discoveries of new blending agents, all are ready to contribute to the production of the highest quality of aviation fuel on a scale impossible of attainment and indeed undreamed of a few years ago. Not content with the revolutionary results already arrived at the research workers are developing in their laboratories variously named products with octane numbers well above 100 and will have these ready when engines are designed capable of using them.

This is only one phase of the progress which the oil industry is making in many directions in the improvement of established products and the development of new ones, but in the present juncture of world affairs it becomes a factor of enormous significance.



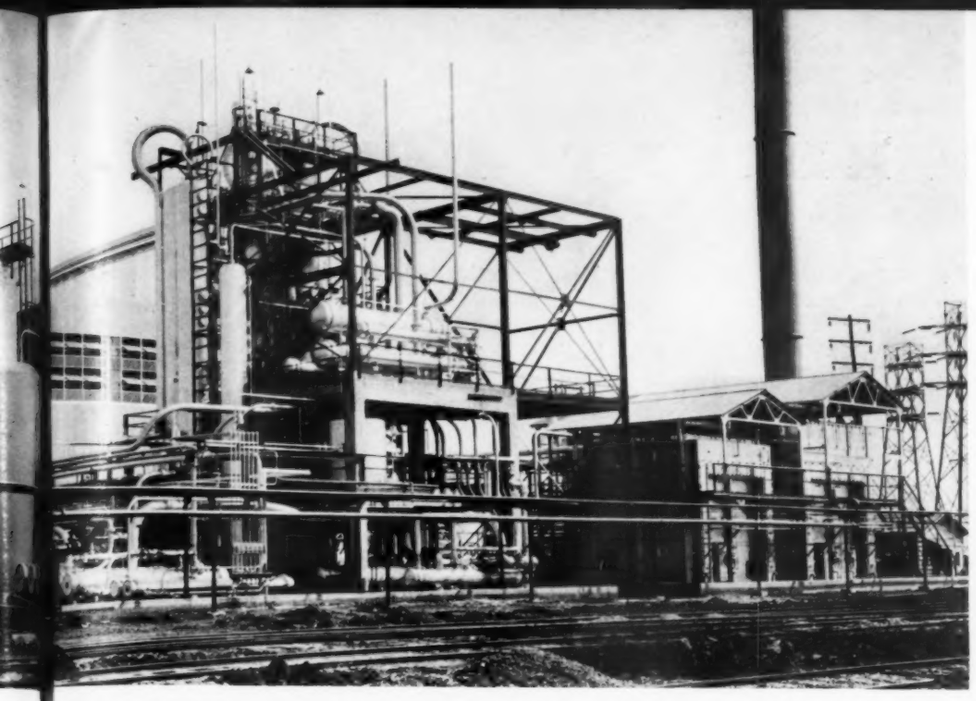
The world's most l[arge] Coast to Coast now re[quires] [con]stant

EXPANDING WAR NEEDS FACE REFINING INDUSTRY

U. S. Armament Program and Operation of Lease-Lend Act Call for Plant Extension and Greater Output of High Octane Gasoline.

WHEN the first definite move toward the strengthening of American defensive power was made, early in 1940, a hasty survey was made of the industrial resources of the nation and estimates were prepared of the probable demands of the defense program upon different lines of industry. In the case of oil it is interesting to note the extent of the anticipated requirements imposed by the defense program as projected at that time. In view of the emphasis placed on the expansion of the land, sea and air forces of the nation, all dependent on petroleum for their propulsion, it was estimated that a ten percent increase in crude oil production from the 3,500,000 bbl. daily which was the average output at that time would be needed. This estimate took into account not only the direct requirements of the defense establishment but also the expected increase in commercial demand foreseen as a result of increasing industrial activity. In this connection it may be noted that the actual rise in production has been somewhat greater than the ten per cent estimated since production is now running slightly above 4,000,000 bbl. daily. One of the important needs contemplated by the original defense program was a much greater quantity of aviation fuel and it was proposed that the daily production of 20,000 bbl., which then was considerably in excess of current consumption, should be raised to 40,000 bbl., a figure which now has been exceeded. Doubling the size of the navy obviously called for double the quantity of fuel oil which then was being consumed at the rate of about 9,000,000 bbl. per year. This, however, was such a small fraction of the yearly production of 350,000,000 bbl. of heavy fuel oil that enlarged naval needs obviously could be met without serious effect on the general supply situation. The main increase in the demand for residual fuel oil, it was rightly anticipated, was to come from the expansion of industrial activity. Actual consumption of this class of fuel has exceeded production only to the extent of reducing stocks by eleven percent.

In performance since the inception of the defense program the oil industry has met greatly increased demands for its products and has done all that was expected of it. It has accomplished this through the operation of its established organization and has made good its claim of preparedness to meet whatever demands might be put upon it by the needs of the defense program as outlined. What the industry was not told a year and a half ago, for the reason that it could not be foreseen by those who shaped the original preparedness plans, was that it would face heavy additional drafts upon its supplies with greatly reduced transportation equipment. As originally conceived the projected armament expansion was a purely defensive program, designed to assure American security and to provide protection for the country's coasts and shipping. Since that time national policy, influenced by the course of the war, has undergone several changes. Acquisition of numerous naval bases in the Atlantic and decision to build a two-ocean Navy enlarged prospective demand for petroleum in one direction while expansion of the plane building program extended it in another. Enactment of the lend-lease law marked another definite shift in



veloped refining industry stretching from the Gulf to Canada and from bstantial expansion to meet the tremendous demands of modern warfare

policy. Transfer to the western hemisphere of the task of supplying all of Britain's war requirements greatly increased export demand for aviation fuel and lubricants. From a purely defensive role the United States assumed the task of serving as the arsenal of democracy.

As a direct consequence of heavy shipping losses and rising war demands a large section of the United States tanker fleet was withdrawn from its regular Gulf-Atlantic service to aid in the movement of oil to Britain. Coming at a time when domestic demand was exceptionally heavy the question of transportation, which until then had not been troublesome, suddenly became critically important. To meet the changed situation it was necessary for the oil companies to revise schedules previously set up and to direct their energies to finding substitute means of moving products to the places where they were needed. When Germany carried the war into the Soviet Union another major change in the situation took place. This was due to the decision to extend aid to Russia, one of the most urgent forms of assistance needed being gasoline for Soviet planes. This imposed a further load upon the rapidly mounting requirements for this particular product. During the period while these changes in the war situation were occurring the plans of the United States as to its own armament and its relations to the active participants in the struggle were undergoing repeated revision with as frequent increases in its demands upon the oil industry, as upon all others directly concerned in the war effort. Earlier estimates as to the quantities of steel, aluminum, copper, rubber and other essential materials required by military, naval and aerial needs were so far exceeded by the development of these plans that a shortage of materials and manufacturing capacity was threatened, and the oil industry, like a hundred others, was faced by difficulties in obtaining metals and machinery to carry on the enlarged scale of operation foreseen as likely soon to be required of it.

In considering the place that petroleum holds in the nation's war effort it must be borne in mind that the tasks which it is being asked to assume today and the problems it is called upon to solve are not the same that were put before it in May and June 1940. The industry has been steadily under the necessity of raising its sights, enlarging the scope of its plans for expansion and adjusting itself to changes in conditions that have taken place almost overnight. Like the battle front itself the industrial front has had to conform to rapid shifts in tactics and objectives. Not only have great changes taken place in the demand for particular products but even the definition of some of these products has been altered. Until this year gasoline of 87 octane and higher was classed as aviation fuel and official statistics have continued to be compiled on this basis. Commercial air liners used 87 octane; for training purposes the Army and Navy specified 91 octane; only the largest and most powerful military planes were adapted to the use of 100 octane. Today Army and Navy men think only in terms of 100 octane when aviation fuel is discussed. Anything lower is of no practical use under present service conditions, just as the speediest ships of a year ago are outmoded in the rising tempo of aerial warfare. Gasoline stocks of less than 100 octane rating and the published statistics of such supplies provide no reliable indication of the available quantity of the grade that is being called for by the belligerent nations. Hence the urgent appeals to multiply the output of top grade aviation fuel.

Controversy over the probability of a gasoline and fuel oil shortage in the eastern states during the coming winter has received much publicity in the daily press. While some oil company officials admit that a combination of severe cold weather and further tanker transfers might reduce working stocks in eastern territory to dangerously low levels it is not anticipated that motorists or users of heating oil will be put to any serious inconvenience. Reasonable curbs upon avoidable consumption are relied upon to meet the situation. Since the products involved are not those most in demand to meet the war emergency there is no immediate prospect of a collision between the two programs. A tight situation may develop, however, in the provision of aviation fuel and lubricants to meet rapidly mounting war aid needs. If this does occur it will arise, not from a lack of the oil industry's supply of raw materials and processes but from the time required for the construction of plant and equipment. This is the factor that makes the question of priorities the all-important problem for oil men at the present time.

Because of its efficient organization and great reserve capacity the oil industry has been able thus far to meet the unforeseen demands that have been put upon it. One reason for its success in this direction is to be found in the fact that in certain respects the thinking and planning of the industry has been in advance of that displayed by those having official connection with the defense program. Several oil companies have made heavy investments in alkylation and iso-octane units without formal assurance of a market for their products but in the belief that demand would develop by the time the plants could be put into operation. The same applies to toluene and butadiene installations. This display of foresightedness will be of greatest assistance to the government in its efforts to meet the heavier obligations that it now has undertaken. Intensification of the world conflict will put a heavier strain upon the oil industry in 1942 than it has undergone thus far and there is nothing in sight to indicate that the load will not continue to grow in 1943 and perhaps in years beyond that. The industry has the resources, the methods and the technical knowledge to meet these demands but it must have freedom of action and access to materials needed for enlarged production. Refining operations are now close to capacity except for obsolete plants that would be of little value in providing the high quality special products that are most urgently needed.

Primary requisites for keeping the output of petroleum products abreast of future demands are the concentration of effort upon the expansion of facilities for the production of fuel, lubricants and explosives for the war machine and a priority system that will assure the materials for plant maintenance and new construction. Under the most favorable conditions time is required for the fabrication and erection of the equipment for large scale refining operations but with adequate allowance for this factor the industry can paraphrase the celebrated utterance of Prime Minister Churchill and say: "Give us a chance to get the tools and we will do the job."

TRENDS IN RECENT REFINING

Present Day High Speed Transportation Rests on a Foundation of Petroleum and Automotive Research—The Accompanying Article Reviews Major Developments and Their Effect on Modern Transportation.

THE modern passenger car glides noiselessly by, the Diesel streamliner streaks across the prairies at sustained high speed, and the silvery stratoliner spans the continent from dusk to dawn. Each in its respective field is a masterpiece of engineering skill and the world pays tribute to the genius of the research, engineering and production groups in the automotive industry which have made possible the modern era of high speed transportation. Power plants of these land and air borne units require liquid fuels of ever-improving quality, and would operate at greatly reduced efficiency, if at all, on the fuels and lubricants of 20 years ago.

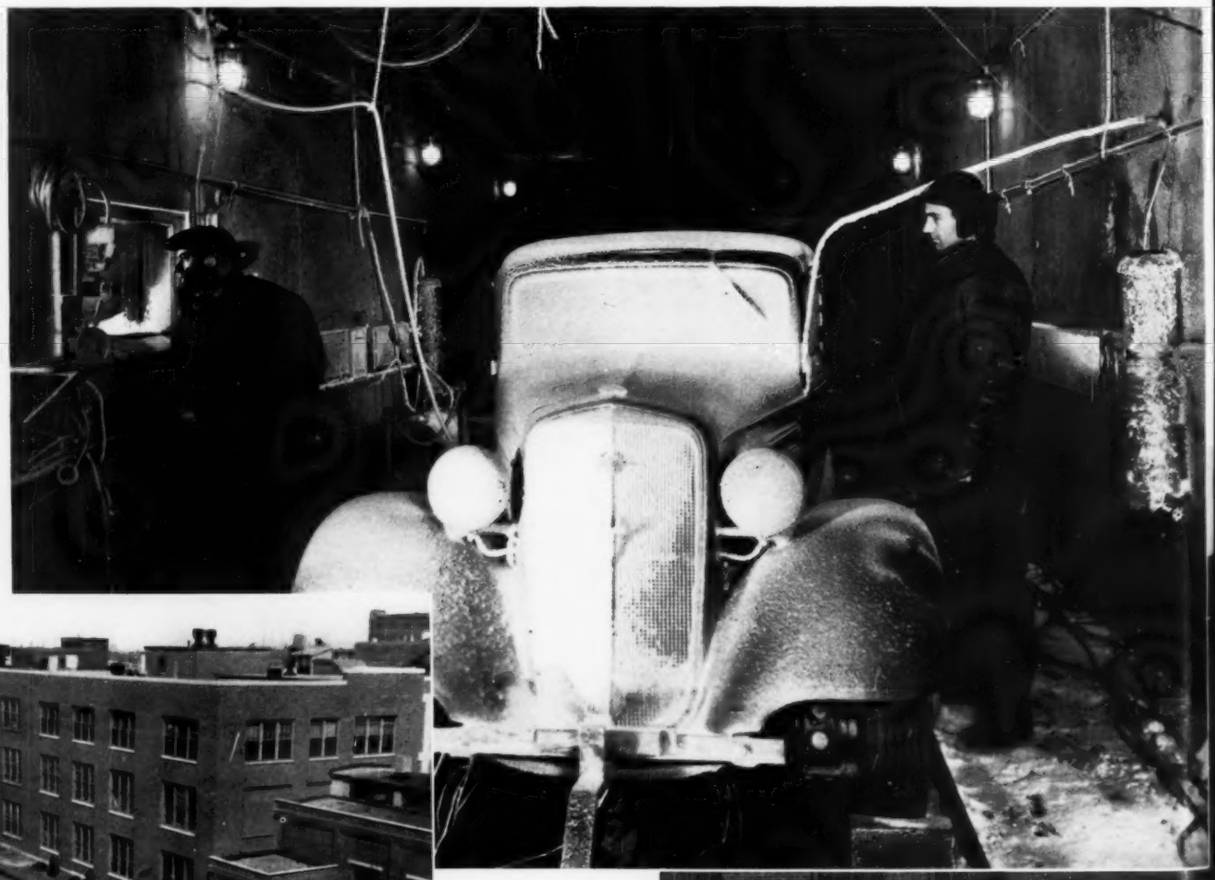
Research and engineering staffs of the automotive, Diesel, aviation and petroleum industries have worked in close collaboration in development of auto and Diesel cycle engines, so that as each advance in engine design brought forth more flexible and efficient power plants, the petroleum industry was ready to supply improved fuels and lubricants required for maximum performance and economy of operation. The contribution of petroleum research to improved production and manufacturing methods has been the subject of numerous technical papers over the past two decades. This paper, therefore, will review rather briefly major developments in the petroleum field and their effect on modern transportation through the medium of improved fuels and lubricants suitable for present-day engines.

Successful completion of the first oil wells some 80 years ago was followed by a slow but steady increase in crude oil production to a figure of 63,000,000 bbl. in 1900. With the increase in automobile production immediately following the World War, and continuing at an accelerated pace during the 1920's and 30's, requirements for crude grew tremendously so that United States production reached 1,264,000,000 bbl. in 1939, a twenty-fold increase over 1920. This increased demand for crude over the past two decades has led to many predictions that the United States crude oil supply was nearing depletion, but production research has enabled the industry to add to its crude reserves at such a rate that over the past few years additions to reserves have exceeded the amount of crude consumed. These reserves have grown from an esti-

Photographs accompanying this article were taken by John Hall for Esso Laboratories.

Right, in this temperature control room it is possible to produce a reading of 40 deg. below zero. Oil, fuel and lubricant performance are checked carefully at such temperature.

Below, one of the buildings of the Esso Laboratories, Standard Oil Development Company at Bayway, N. J.



RESEARCH

mated 5,000,000,000 bbl. in 1925 to approximately 19,000,000,000 bbl. in 1940.

Production research calls upon engineers, geologists, geophysicists and chemists in its program of conservation and exploration. Technical staffs of producing companies have made great strides in locating new fields and oil deposits, and in spite of the necessity for ever deeper drilling and decreased surface indications of oil, have maintained the percentage of oil producing, gas producing and dry wells at approximately 70-62 percent, 8-10 percent and 21-24 percent, respectively, over the past two decades. Application of research to production has contributed to more efficient recovery from producing wells by means of gas repressuring, controlled flow, acidification, water flooding and better well spacing. Improved drilling technique and better drilling tools have likewise contributed to more efficient oil recovery and lower drilling costs. Certain deep deposits which could not have been reached by drilling technique of the early 20's can now be tapped by modern drilling machinery, and wells of 10,000 to 12,000 ft. are not uncommon. These deep wells can now be drilled at an average cost of $3.00 to $4.00 per foot for 4,000 to 6,000 ft. wells against an average cost of $8.00 per foot by older drilling methods for 3,000 to 4,000 ft. wells. Thus, it can be seen that petroleum research has not only permitted the industry to withdraw much greater quantities of crude but at the same time has built up reserves, so that the industry is not faced with any immediate depletion of its basic raw material.

Some thirty years ago, about the time production of motor cars commenced its steady climb, the U. S. refining industry was able to obtain about 10 to 15 percent of motor gasoline from crude. With increased acceptance of the automobile as a means of transportation, yield of gasoline from crude became the major problem of the petroleum industry. Since increased production of gasoline meant heavier demands on crude reserves and increased inventories of heavier distillates for which no ready market existed, research was, therefore, directed towards increasing recovery of motor gasolines from crude. Initial progress was slow and as late as 1921 straight-run fractions from crude and natural gasolines accounted for about 76 percent of the 140,000,000 bbls. of gasoline produced. Throughout the 1920's and 1930's the industry made ever wider application of various cracking methods developed by its research laboratories, with the result that the amount of cracked gasolines increased rapidly and in 1936 the percent of cracked gasoline in average motor fuel equalled the virgin fractions. Modern cracking units are now capable of producing 65-75 percent of gasoline from crude, but due to heavier demands for heating oils, kerosenes and other higher boiling distillates, U. S. refining industry is now averaging in the neighborhood of 45-46 percent of gasoline on crude.

Present day cracking research, dealing as it does with reactions involving temperatures of 800 to 1200 deg. F. and pressures as high as 1,000 lbs. per sq. in. or more, utilizes the services of chemists, engineers, and to an ever increasing extent, calls upon the metallurgists for better metals of construction. As improved alloys are made available, petroleum technologists have generally been eager to increase the severity of cracking conditions up to safe working limits of new materials.

Modern thermal cracking technique not only increases recovery of gasoline from crude but permits the refiner to control quality of motor fuels. By choice of cracking conditions the refiner can vary volatility of his gasoline by controlling the ratio of low to high boiling components, and can also exercise some control over chemical characteristics of the fuel by increasing the branchiness of paraffins and the amount of olefins or aromatics, which in turn increase anti-knock value of fuel with its resultant influence on modern motor design. Thermal reforming, although utilizing basic principles of thermal cracking and used in conjunction therewith, is mainly concerned with improving fuel quality rather than obtaining greater gasoline yields from crude. The reforming operation on relatively low-octane heavy naphthas results in lowering boiling range of feed stocks and, by a series of reactions involving splitting, dehydrogenation, isomerization and aromatization, raises anti-knock value of the feed as much as 25-30 octane numbers. The combined effect of thermal cracking and reforming has been directly reflected in octane rating of motor fuels available over the past decade. In 1939 the average A.S.T.M. octane rating of U. S. gasolines was slightly over 60, while in 1939 it had risen to 72. During this same period compression ratios of American automotive engines have risen from 4.7 to 6.3. Here we have an example of benefits to be derived from cooperative research and development in closely allied industries as the octane ratings must progress in relation to compression ratings.

Test cars used in fuel and lubricant research.

Until the last few years, commercial hydrogenation was limited to the use of essentially pure hydrogen at fairly low pressures, catalysts of the reduced nickel type, and operating temperatures well below thermal decomposition temperature of the feed stocks. Coal tar and petroleum fractions, which contain appreciable quantities of sulphur, poisoned the nickel catalysts so that the process was mainly limited to hydrogenation of high purity organic compounds, sulphur-free hydrocarbons, and animal and vegetable oils. The classic research of Bergius on sulphur resistant catalysts, later developed by I. G. Farbenindustrie and applied to petroleum hydrocarbons by the Standard Oil Development Company, has given the oil industry one of its most flexible processes for production of motor fuels from cracked and virgin gas oils; high octane aviation gasolines from kerosene and gas oil fractions; aviation blending agents by saturations of branched chain polymers; high grade Diesel fuels from low boiling gas oils; high flash, high octane safety fuels, and low sulphur and highly stable gasolines from high sulphur, unstable distillates.

In the preparation of high octane motor and aviation gasolines, the extent of hydrogenation is controlled by choice of operating conditions and catalysts to give minimum hydrogenation consistent with stability of aviation gasoline. By recycle operations gasoline yield of 85 to 95 percent are obtained, the remainder of the feed going to light liquid products or gas. With most feed stocks considerable quantities of isobutane and isopentane are produced along with aviation gasoline. The excess isopentane produced can be utilized for blending with high octane number materials, such as alkylate or hydro codimer, to improve their volatility. The isobutane produced can be used as one of the raw materials for alkylation to make high octane number blending agents. Motor and aviation gasolines produced in this operation are predominantly naphthenic and isoparaffinic; have extremely low sulphur and olefin contents, high chemical stability, high unleaded octane values and excellent lead susceptibility for high octane finished products.

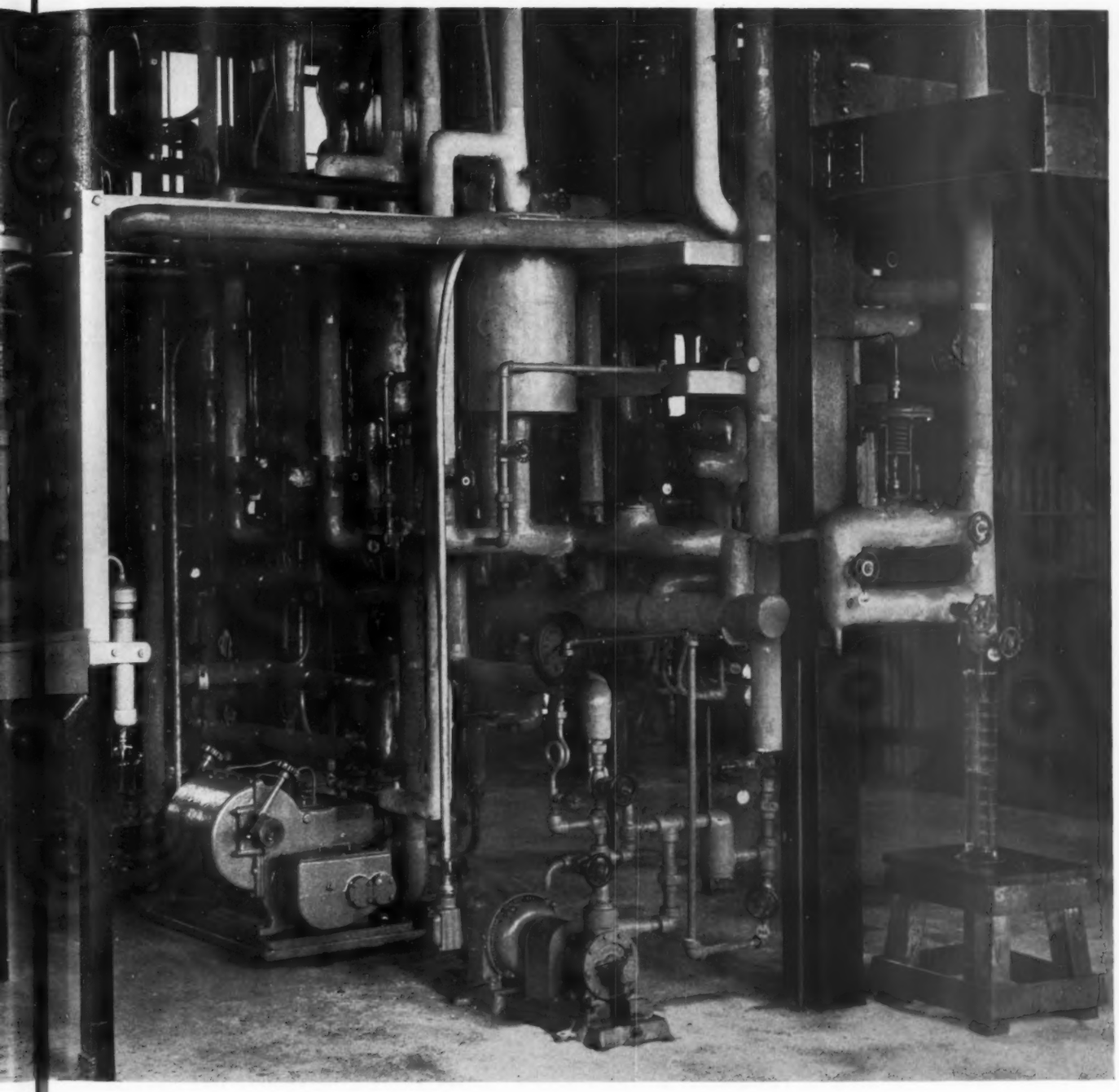
The hydrogenation process not only offers the refining industry a means of obtaining high yields of superior motor fuels from gas oils and other feed stocks which cannot be economically converted into acceptable products by thermal means, but produces high quality aviation fuels from light gas oils and low quality kerosenes. Hydrogenated aviation fuels have the same or better chemical stability than straight-run aviation gasolines, clear A.S.T.M. ratings ranging from 75 to 77 and high lead susceptibility. They are excellent base stocks for use in production of 100 octane gasolines since their high clear octane ratings and excellent lead response result in appreciable savings in blending agent requirements for any given octane and lead concentration.

The hydrogenation process is also utilized in saturation of high octane polymers for use as aviation blending agents. Diisobutylene, the product obtained by polymerization of isobutylenes; or codimer, the cross-polymer of iso and normal butylenes, have octane ratings in the region of 82-85 A.S.T.M. but on account of their unsaturation and low lead response cannot be used in aviation fuels. Octane ratings of these same products after hydrogenation are raised to the 95-99 A.S.T.M. level and lead response is greatly improved. These hydrogenated products, until recently, were the only source of blending agents for leaded aviation fuels of 100 octane number or higher now so much in demand for civil and military aviation.

Until the last few years all heavier distillates and residues were transformed into lower molecular weight hydrocarbons by thermal cracking or hydrogenation. In an attempt to obtain less degradation to tars and to reduce the amount of fixed gases and highly volatile light liquid products resulting from thermal operations, a number of research groups initiated work on the application of catalysts to the cracking reaction. These research efforts have borne fruit as shown by numerous installations of the fixed bed catalytic process and several plants now under construction which will utilize fluid catalytic cracking technique. Each of these processes, due to milder operating conditions employed and beneficial effect of catalysts, gives higher yields of high octane gasoline than have heretofore been possible by straight thermal operations. The effective octane blending value of catalytic gasolines makes available to the refining industry an economic method of improving anti-knock value of the gasoline pool.

In the fixed bed type of catalytic cracking the operating cycle is intermittent. Vaporized feed is passed over the catalyst and the cracking cycle is continued until the catalyst begins to lose activity due to deposition thereon of carbonaceous materials. The reactor is then purged of hydrocarbons and the catalyst regenerated in place by passing air or a controlled mixture of air and inert gas through the catalyst bed. After the regeneration step, the unit is again ready for the cracking cycle. Commercial fixed bed installations employ several of these reactors with common feed vaporizing and product fractionating systems. By means of an automatic valve timing system, feed can be switched from one reactor to another, thereby obtaining continuous operation of the unit. In fluid catalyst operation the catalyst flows through the reactor and regeneration systems admixed with feed and regeneration gases, respectively. In the cracking cycle the catalyst meets the feed, passes through the reaction chamber where cracking occurs, and the cracked product and catalyst flow from the reaction through a catalyst recovery system to fractionating equipment. The catalyst disengaged in the recovery system flows to the regenerator where carbonaceous deposits are burned off. The regenerated catalyst is then returned to the cracking section to repeat the cycle.

While catalytic cracking plants will normally find their greatest utility in the production of high quality motor fuels, either process may be employed in production of aviation gasolines. These aviation fuels, even though they contain small amounts of olefinic compounds, can be made gum stable and have been used with success. The high anti-knock value of catalytic cracked aviation gasolines, coupled with high lead susceptibility, makes them distinctly valuable as base stocks for 100 octane aviation gasolines. Catalytic cracking processes are a contribution to national defense in extending supplies of high octane base stocks and in permitting production



Phenol extraction pilot unit of the Esso Laboratories, Standard Oil Development Company.

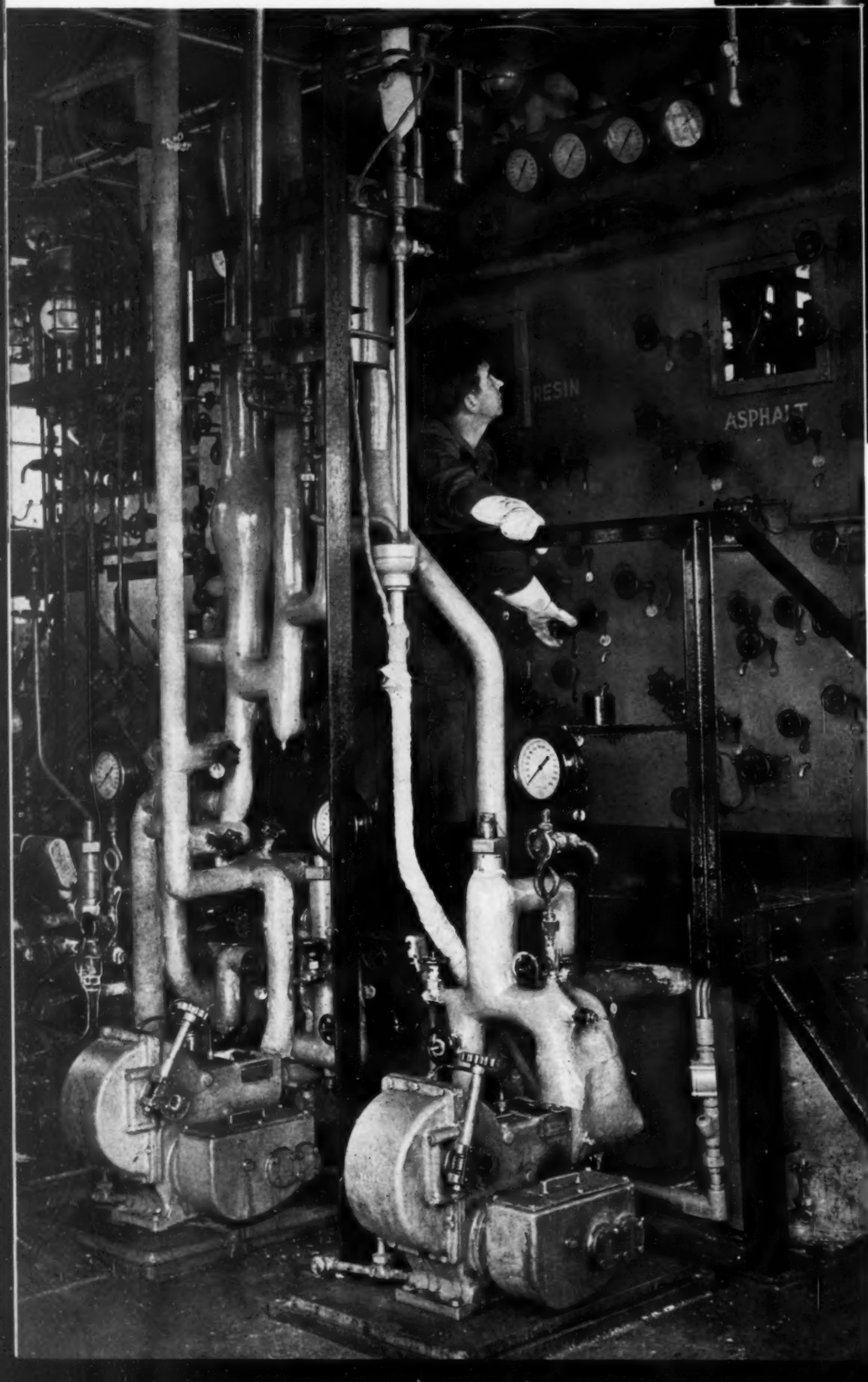
of the maximum amount of 100 octane aviation gasolines from existing supplies of blending agents. Catalytic reforming processes have recently been developed for improving the quality of heavy naphthas. These processes yield high octane, low sulphur reformates with less change in volatility of feed than would be obtained with corresponding thermal reforming. Yields of reformate are usually higher than those obtained by the best thermal methods since there is little tendency toward degradation of the feed to butanes and lower constituents. By proper choice of operating conditions and catalysts, the catalytic reforming reaction mechanism can be predominantly dehydrogenation or aromatization. Under the former conditions six carbon atom naphthenes can be dehydrogenated to corresponding aromatics, while in the latter, straight chain paraffins can be cyclized. The catalytic reforming process is of vital importance to national defense since it can make available adequate supplies of aromatics for all military purposes.

Synthesis of isooctane by Dr. Edgar and his associates at the Ethyl Gasoline Corporation laid the groundwork for present methods of rating motor and aviation gasolines. For several years isooctane was a laboratory chemical and found its main use as a primary reference standard for anti-knock determinations. Some seven or eight years ago research workers in the petroleum industry found a simple and economical method of polymerizing selectively isobutylenes to the dimer which on hydrogenation yields the saturated branched chain paraffin 2,2,4-trimethyl pentane (isooctane). Research workers immediately set to work to try to cross-polymerize isobutylene with normal butylenes since they recognized that yields of high octane blending agent could be doubled by the copolymer route. Two selective polymerization processes—the U.O.P. phosphoric acid and the Shell-Jersey hot sulphuric

acid process—were quickly made available to the refining industry and, until the advent of alkylation, furnished all the high octane blending agents used in production of 100 octane fuels.

Hydrogenated codimers of iso and normal butylenes have clear octane values ranging from 95 to 97 which is only slightly lower than the 99 to 100 octane product obtained by hydrogenation of diisobutylene. The debutanized hydrogenated codimer is completely saturated, boils between 190 and 250 deg. F. and has a mid-boiling point of 228 to 230 deg. F. This high mid-boiling point, coupled with a Reid vapor pressure of about two pounds, allows the addition of isopentane as a vapor pressure and volatility corrective agent before blending with the average base stocks for 100 octane fuels. In general practice, the hydrogenated codimer is elevated to seven pounds Reid vapor pressure with isopentane and this blending agent of approximately 95 to 96 octane is blended with a seven pound Reid vapor pressure base naphtha for the 100 octane base. Concentration of blending agent varies with octane rating and lead susceptibility of the base naphtha and, as pointed out previously, appreciable savings in blending agents are realized by substituting hydrogenated or catalytic cracked aviation naphthas for the average straight-run aviation base stock.

Effect of these processes and the alkylation process, which will be discussed in a later paragraph, on military and civil aviation is readily apparent by comparing performance of high output aviation engines on fuels of 87 and 100 octane ratings. By going from 87 octane to 100 octane, it is possible to effect a 15 to 30 percent increase in take-off power or rate of climb and a reduction of 15 to 20 percent in fuel consumption under cruising conditions. Improved take-off power is vitally important in the case of heavy transport planes and bombers, while increased rate of climb is a requisite for fighting plane perfor-



Right, hydraulic tensile testing machine used in testing materials of construction; research laboratories maintained primarily for petroleum research, also fulfill other important functions for the industry. Below, propane deasphalting pilot unit of the Standard Oil Development Company.

mance. Decreased fuel consumption at cruising speeds has contributed in no small way to development of long distance, overseas flights, and in the case of long range bombers now in production, may mean the difference between successful completion of the bombing mission or forced landing in enemy territory.

Several non-selective polymerization processes for utilizing propylenes and butylenes are now available to the refining industry. These processes, in contradistinction to selective processes, are mainly used in production of polymers for upgrading motor gasolines, since on hydrogenation octane ratings of non-selective polymers are usually degraded from 85 to 86 A.S.T.M. to 75 octane or slightly higher. In motor gasolines non-selective polymers have octane blending values from 95-110, depending upon the octane of the base gasoline, the ratio of propylenes and butylenes in the feed to the polymerization unit, and concentration of polymer in the blend. These non-selective polymerization units are not limited in utility to large refineries and plants of from 30 bbl. to 100 bbl. are in common use. In some of the larger refineries, however, 2400 bbl. a day plants are in operation. Non-selective polymerization is an effective means of converting unsaturated low-boiling olefins, which cannot be incorporated in motor gasolines, into high octane blending agents which can be blended into the refinery gasoline pool to raise the over-all octane.

Thermal polymerization is another process which has been made available to the refining industry whereby propylenes and butylenes, as well as field propanes and butanes, can be converted into blending agents for motor gasoline. This process employs pressures ranging from 1,000 to 3,000 lbs. and temperatures in the region of 950 to 1100 deg. F. The thermal polymerization process, which in reality constitutes a combination of cracking and heat polymerization, is of greatest economic value in large refining units having excess propane and butane or those having access to low cost field butanes and propanes. The product obtained by thermal polymerization is of high octane number and like the non-selective catalytic polymers, cannot be hydrogenated for use as aviation blending agents.

Petroleum technologists were quick to recognize that selective polymerization did not yield a maximum amount of blending agent from refinery olefins. The average refinery butane cut contains about two parts of normal butylenes to one part isobutylene and, since selective polymerization is a direct linkage of isobutylene with an equivalent amount of normal butylenes, large quantities of excess normal butylenes were left over which had to be discarded to fuel or non-selectively polymerized with propylene to produce blending agents for motor gasolines. It was further realized that, if some means could be found of condensing isobutane with iso and normal butylenes, the yield of blending agents from available olefins could be extended many fold. Previous work had indicated that this direct coupling would be feasible with metallic halide catalysts, but catalyst consumption was too high to permit economic commercial application. Research staffs of the Anglo-Iranian Oil Company, Ltd., The Humble Oil and Refining Company, Shell Development Company, The Texas Company and the Standard Oil Development Company worked out alkylation processes involving sulphuric acid as the catalytic agent.

The alkylation process may be pictured as follows: Admixture of olefins with strong sulphuric acid yields an alkyl sulphate as a primary reaction product. This ester in the presence of the large excess of isoparaffin couples with relatively inert saturate to form a branched chain higher molecular weight paraffin. In the case of butylenes and isobutane, the principal reaction products are highly branched octanes. By this relatively simple catalytic process the yield of branched octanes is about seven times that obtained from cold acid polymerization and from two to three times that from hot acid or U.O.P. selective polymerization processes. In certain cases where isobutane is limiting, the selective polymerization process is used to polymerize the iso with an equal quantity of normal butylene and excess normal butylenes are alkylated with isobutane. Thus, the two processes are economically complementary and under certain conditions may be employed to obtain maximum yield of aviation blending agent from available olefins. Propylene and pentenes may also serve as olefins for the alkylation reaction, but octane ratings of the alkylates obtained are usually three to five points lower than butylene alkylates. As in the case of hydrogenated butylene polymers, mid-boiling points and vapor pressures of butene and pentene alkylates do not meet aviation gasoline specifications, so that isopentane is usually used as a fill and vapor pressure agent. Propene, butene and pentene alkylates can all be used in the manufacture of 100 octane fuels. The amount of blending agent required varies from 50 to 70 percent depending upon the alkylate and octane value and lead susceptibility of the base gasoline. Ready acceptance of alkylation by the refining industry is shown by some twenty alkylate plants in the United States and foreign countries, which have an output of well over 7,000,000 bbl. per year of blending agent.

Another alkylation process developed by Phillips Petroleum Company links ethylene with isobutene by purely thermal means. Operating temperatures in this process are in the region of 900 to 1000 deg. F. and system pressure varies from 3,000 to 5,000 lbs. per sq. in. The principal reaction product, accounting for about 40 percent of total liquid yield, is neohexane. Neohexane has an A.S.T.M. octane value of about 94 to 95, favorable volatility characteristics and good lead susceptibility. These characteristics make it valuable as an aviation blending agent in combination with isoctane, alkylates and isopentane.

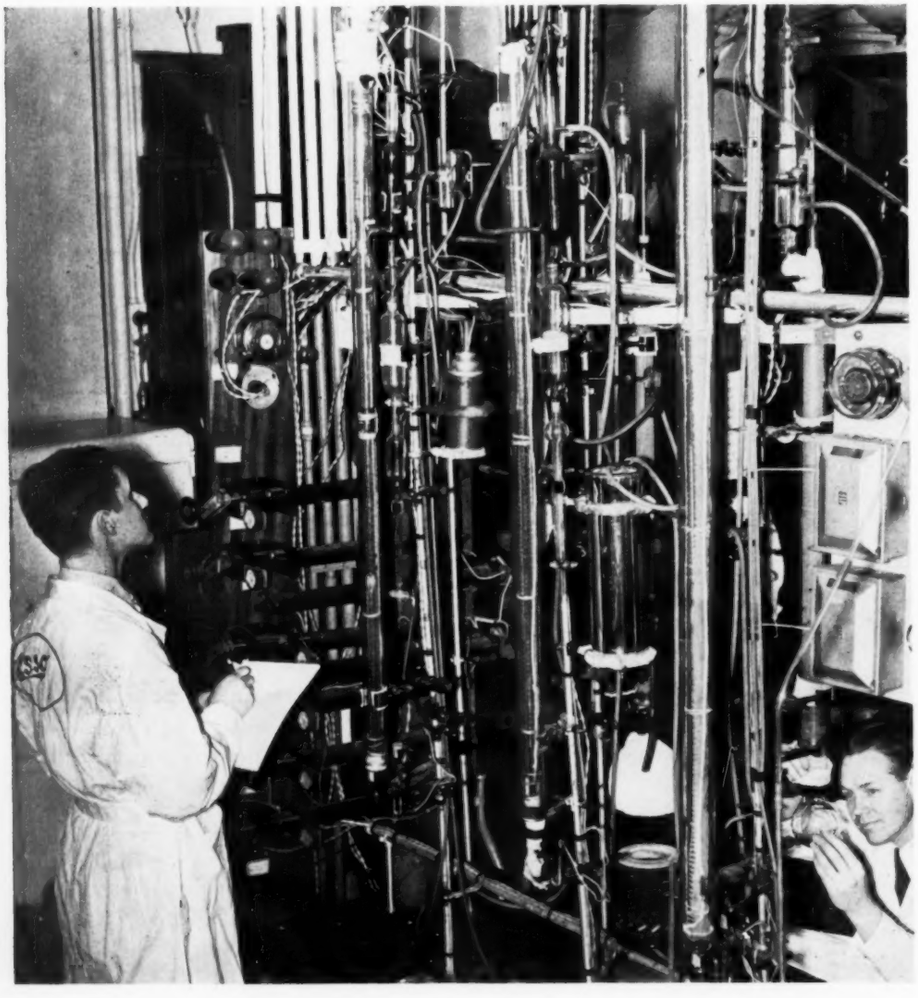
With the advent of more severe thermal cracking and reforming, the refining industry was faced with an entirely new problem, namely, the instability and a tendency toward self-polymerization of unsaturates in cracked distillates. Petroleum research has met this challenge by improved acid treating techniques, clay treatment and new sweetening processes. In addition to these processes, powerful inhibitors have been developed which retard or eliminate gum deposition in storage or in the induction system of the modern engine. Thus, research has been able to provide methods for reducing treating losses, maintaining octane ratings and lead susceptibility, and in guarding against possibility of gum formation after the fuel leaves the refinery.

In preceding paragraphs achievements of fuel technologists in providing suitable liquid fuels for high output automotive and aviation engines has been outlined. Just as the efficiency of the modern engine would be severely reduced by the fuels of two decades past, lubricants of that period would have limited engine development had not petroleum research been able to produce lubricating oils which met ever increasing quality requirements as power output of automotive and Diesel engines increased. Lubrication research was first directed towards improved distillation and treating techniques, while in the last ten years these efforts have been directed towards segregating higher quality lubricating fractions, lowering manufacturing costs and producing high quality aviation, motor and industrial lubricants from crudes which had heretofore not been con-

sidered suitable sources of lubricating oils. Modern engines require lubricants which will flow freely at zero and sub-zero atmospheric temperatures yet will not thin out at crank-case temperatures as high as 280 deg. F., nor carbonize on piston crowns, which in heavy-duty bus or truck engines may reach temperatures in the region of 700 deg. F. Research has met this challenge by development of solvent extraction processes to improve viscosity-temperature relationships, and by removal of waxy and other relatively high congealing point constituents through solvent dewaxing. Addition agents have also been developed which, when added in relatively small quantities, raise the viscosity index well beyond that of the best solvent extracted oils from selected crudes. Other additives will lower the pour point of an oil from the usual figure of 10 to 30 deg. F. to well below zero.

Among the solvent extraction processes available to the industry are those employing phenol, nitrobenzene, dichlorethyl ether (Chlorex), propane-cresols (Duosol), furfural and others. Most of these selective solvent processes will raise viscosity of Mid-Continent lube stocks to approximately 100 V.I. and of Pennsylvania lube cuts to as high as 110 to 115. These solvent extracted 100 V.I. oils can be further increased to 115 to 130 V.I. by the addition of small quantities, in the region of five percent of high molecular weight, polymeric linear chain compounds. Several solvent dewaxing methods are now available for reducing the pour point (congealing point) of lubricants, among which might be mentioned propane, benzol-methylethyl ketone, SO_2-benzol and Barisol processes. These processes can economically dewax average lube stocks to pour points in the region of 15 to 30 deg. F. and although lower pour points can be obtained, the operation becomes increasingly expensive as sub-zero pour points are sought. As an adjunct to dewaxing processes, additives are now available which permit the refinery to obtain sub-zero pour points more economically than by intensive dewaxing operations. These pour depressant additives appear to keep the wax crystal small and inhibit its growth, and to prevent adsorption of the oil on the wax crystal. Commercially available pour depressants are high molecular weight, Friedel-Crafts condensation products of aromatics or phenols with chlorinated wax. Other condensation products and voltolized materials have been found effective pour depressants.

One of the most important parts of the Esso Laboratories: column for precise fractionation of petroleum hydrocarbons.

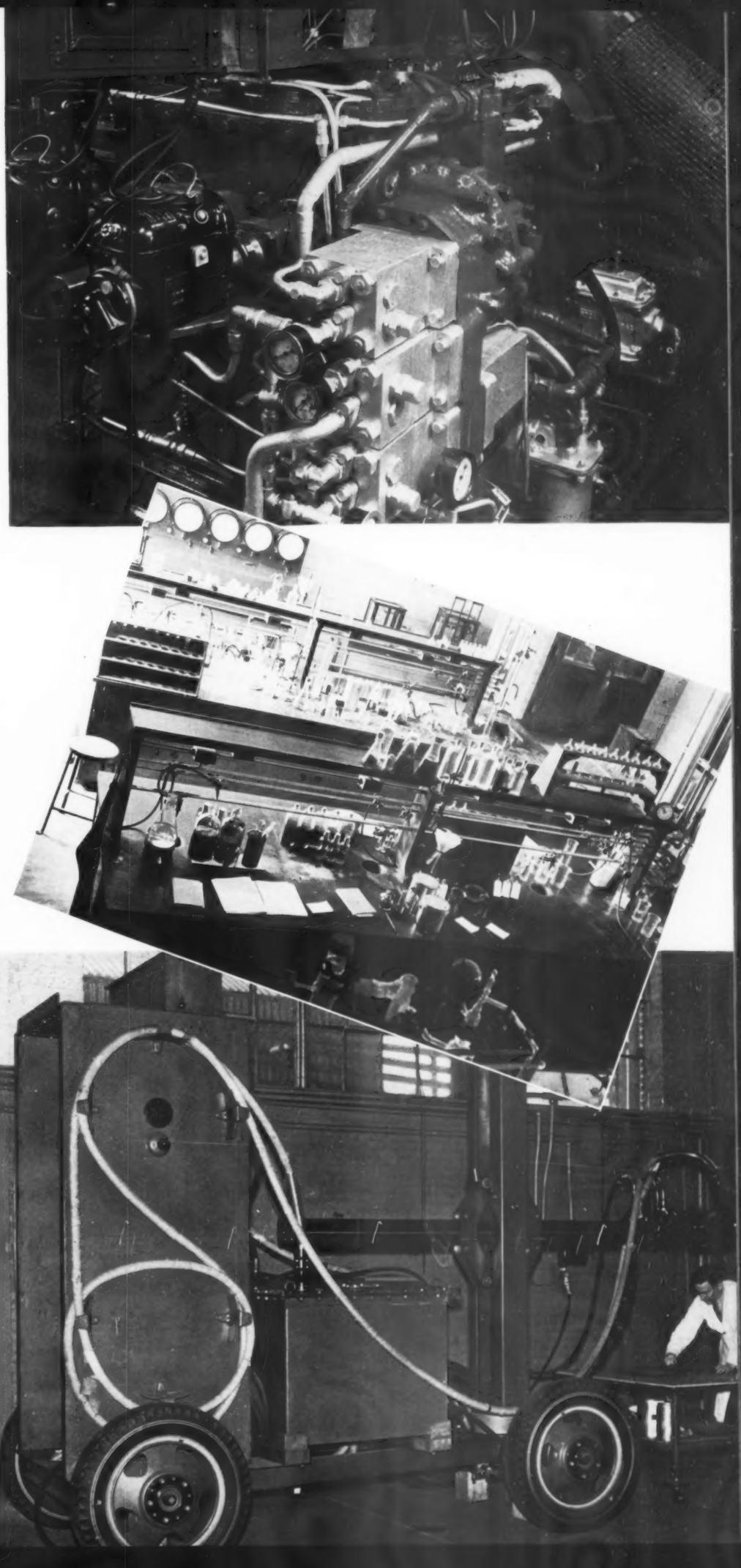


Greater bearing loads in internal combustion engines have led to gradual displacement of babbitt by copper-lead and cadmium-silver alloy bearings. These new bearings, while capable of withstanding much higher bearing pressures, are more susceptible to attack by organic acid. Although new refining techniques have improved the tendency of lubricants to deposit insoluble oxidation products, they do not appreciably improve the oil as regards tendency to form acidic compounds. Moreover, in certain cases where heavy selective solvent treatment is required to obtain favorable temperature-viscosity characteristics, natural oxidation inhibitors may be removed with an attendant increased susceptibility of the lubricant toward oxidation and formation of acidic components. Within the last few years additives have been made available to correct this shortcoming. These additives may function as anti-oxidants, thereby retarding acid formation, or may act as metal pacifiers whereby metal surfaces of the engine are deactivated as regards their ability to accelerate oxidation. Certain substituted phenols are reported to be powerful anti-oxidants. Sulphurized fatty oils and other sulphurized aromatics and substituted aromatic compounds have been shown to be effective anti-oxidants and corroison preventives. Alkyl and aryl phosphates are said to be fairly effective anti-oxidants and also possess appreciable metal pacifying and film strength improving properties. Other additives are now available which have properties known as "detergency" and "dispersivity." By detergency is meant the ability to keep an engine clean by preventing sludge and varnish-like deposits from forming on the engine. By dispersivity is meant the ability of an oil to keep sludge-like material in suspension and to prevent it from settling out on various parts of the engine. Oils having the property of detergency will actually remove, to a certain degree, sludge and varnish-like deposits that have been formed by the use of some other type of oil in prior operation. Oils having the properties of detergency and dispersivity are coming into increasing use for both automotive and Diesel service. For certain types of Diesel service such an oil is essential to satisfactory operation. Multi-functional additives combining pour depressing, V.I. improving and detergent properties have been announced recently. In general, it appears that additives which form stable colloidal systems in lube oils may function as pour depressants, improve viscosity-temperature characteristics and have some sludge dispersing properties. If these compounds contain polar groupings, they may impart added oiliness properties. If sulphur is present in the molecule, they may have bearing corrosion properties and, lastly, if a metal is incorporated in the molecular structure the additive will have some detergent action.

Space does not permit outlining the many im-

provements which have been made in Diesel fuels and special lubricants for automotive and marine Diesel engines. In passing it might be well, however, to point out that the fuel quality required for the high-speed automotive Diesel is a far cry from the old concept that anything which could be injected into the combustion space was good enough for a Diesel engine. The modern automotive Diesel requires fuels which will not congeal at low temperatures, which have a high degree of paraffinicity and low sulphur content. Research has found means of providing these high quality Diesel fuels, and present indications are that, as supplies of virgin or extracted paraffinic fuels decrease, additives can be employed to impart the desirable ignition qualities—so necessary for satisfactory performance—to the more naphthenic fuels.

The contribution of petroleum asphalts to modern transportation is seldom realized. With expanding automotive traffic, the old gravel road soon became obsolete, and various state and county agencies were forced to provide better road surfaces. Although total road mileage has remained fairly constant at approximately 3,000,000 miles over the last 15 or 20 years, bituminous-surfaced roads have increased from approximately 20,000 miles to 200,000 miles in this same period. Improved roads, other than bituminous-surfaced, have remained fairly constant at around 300,000 miles. In 1939 some 30,500 miles of roads were constructed, of which 2,900 miles were of brick or concrete, 11,600 miles were untreated, graded and drained construction, and 16,000 were of the bituminous type. Of special significance to car, bus or truck owners is a recent report from Iowa State College showing comparative costs of automobile operation on three types of roads—paved, gravel and dirt. This report, based on information derived from over 3,000,000 miles of travel by rural mail carriers in year-round operation, who averaged approximately 15,000 miles per year per car, indicated that the cost per mile per vehicle was 3.34c for paved or bituminous-surfaced roads, 4.19c for gravel roads and 4.54c for dirt roads. Asphalt research has made great progress in determining proper characteristics of bituminous materials used in road surfacing operations. Moreover, within the past year, additives have been developed which increase the adhesivity of asphalts towards wet aggregates so that bituminous road construction can now be carried out under the most adverse climatic conditions.



Various phases of the constant research being carried on by the industry that permits it to meet ever increasing demands for more complex products: a Cooperative Universal engine used in testing super aviation fuels; a bench in the laboratory for routine work; and X-ray equipment for testing materials of construction.

EMERGENCY NEEDS CALL FOR HUGE REFINERY EXPANSION

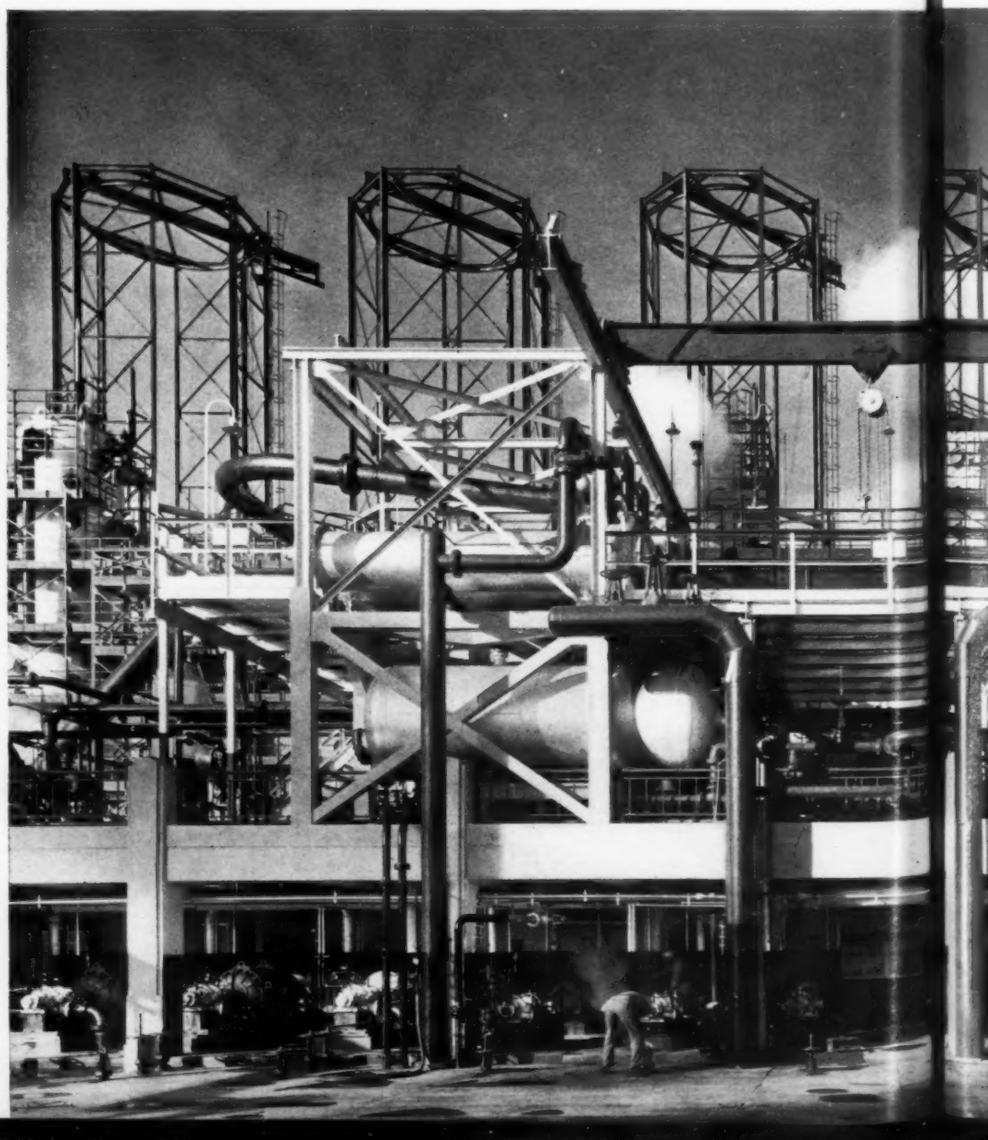
Division of Refining of PCO in Cooperation with Industry Committees Working on Plans for Trebling of 100 Octane Production.

ESTABLISHMENT of the office of Petroleum Coordinator had in view certain definite objectives which were broadly outlined by the President in his order setting up the office. One purpose was to enable the government to be informed as to the availability of petroleum products needed for national defense and war aid and to support the industrial operations essential to the maintenance of these activities. Another was to create an agency that could advise the oil industry as to the needs of the government and aid in the provision of facilities for expanded production wherever such action seemed necessary to aid the national defense policy.

In accordance with the policy thus indicated Secretary of the Interior Ickes, following his appointment as Coordinator, called a conference of members of the oil industry to which he explained that his desire was not to dominate the industry but to work with it and said that the cooperation between the government and the industry should be helpful in solving problems of production and distribution, raising efficiency through united action and keeping such sacrifices as might be necessary as light as possible. To keep the movement on a representative basis and to interfere as little as possible with normal operation a system of regional organization was established. The country was divided into five districts—Eastern, Middle Western, Southern, Rocky Mountain and Pacific Coast. In each of these divisions, district committees were set up for each of the main activities of the business, namely production, refining, transportation and marketing, with a general committee composed of a general district chairman and the chairmen of each of the other four committees. Members of the various committees were appointed from nominees proposed by the industry itself with the object of making the groups broadly representative of all elements in the business. With subcommittees since appointed to deal with special problems in different districts a group of several hundred operating oil men has been assigned to the task of assembling information and enabling the oil industry to function as smoothly and effectively as possible during the emergency.

Proceeding along similar lines the central staff of the Petroleum Coordinator's office is organized into divisions dealing with production, refining, transportation and marketing, with other sections devoted to conservation, research and statistics, exports and other specialized subjects. The organization, which is headed by Ralph K. Davies, Deputy Coordinator, has grown steadily since its establishment and now numbers approximately 175 employees in the central office, including specialists in the various fields of activity mentioned who are drawn from all parts of the country and are familiar with all branches of oil production, treatment and distribution. One of the first moves of the Petroleum Coordinator was to establish a cooperative understanding with other government agencies having to do with the oil situation such as the Office of Price Administration, the Office of Production Management and the Department of Justice. Particularly important to individual oil men was the pronouncement of Attorney General Biddle that in situations where agreements for the pooling of shipments, exchange of products and other forms of joint action were deemed useful in meeting the emergency such procedures, when proposed by the Coordinator and approved by the Department of Justice, would not be made the basis of subsequent action against the participants under the anti-trust laws.

The form of organization adopted, though necessarily extensive in order to cover every part of the country and every branch of oil activity, is relatively simple in the essentials of its operation. It was designed to bring the full power of the industry to bear in meeting emergency demands at home and abroad, to provide governmental protection for forms of joint activity not ordinarily permitted, to assure supplies of mate-



rial for maintaining the essential operations of the industry, to extend assistance where necessary to satisfy defense needs for special products, and to spread participation in the war aid effort over both large and small units in the industry. While time is required to get an industrial machine of such dimensions into full operation its functioning to date is considered satisfactory and the hoped-for cooperation of industry with government has been extended in full measure.

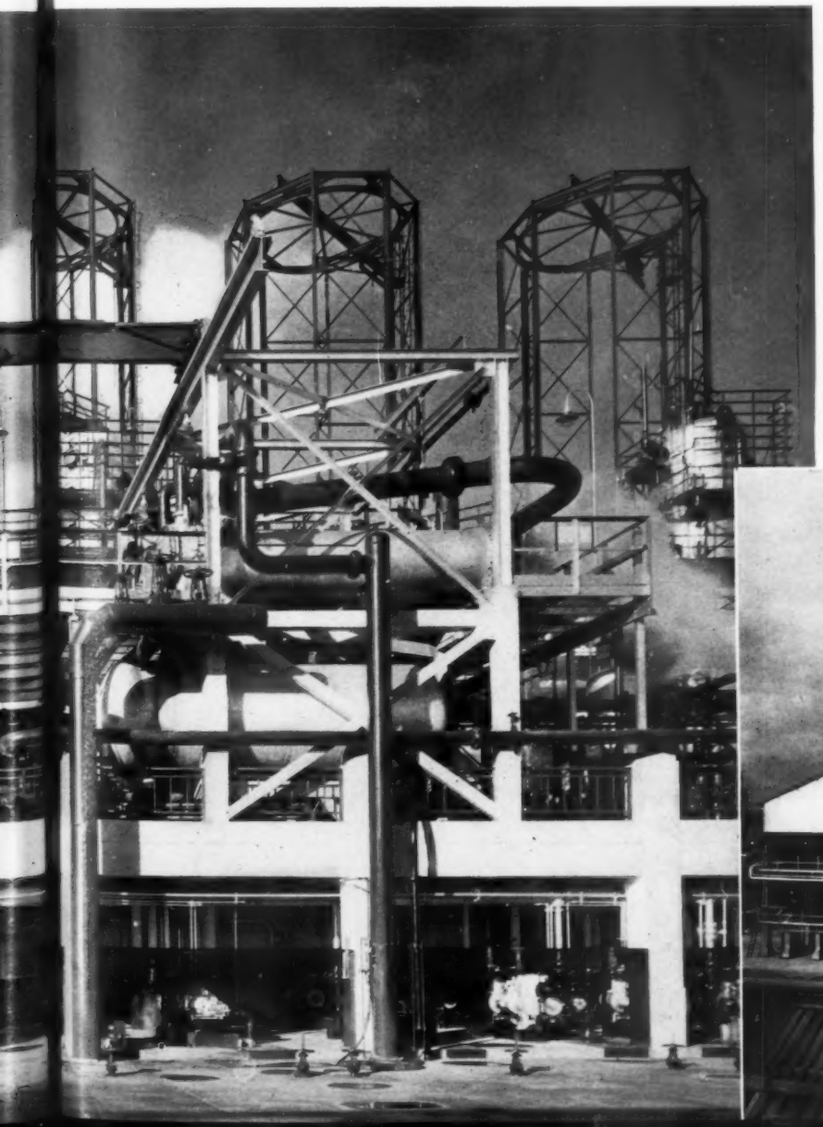
By reason of developments in the areas of war and because of the enlargement of national commitments through enactment of the lend lease law and adoption of the policy of aid to nations opposing totalitarianism the work of the Division of Refining of the Petroleum Coordinator's office and the regional committees working in conjunction with it has assumed special importance. Immediate and prospective demands for certain refined products, specifically for aviation fuel and lubricants, have been multiplied to several times the original estimates of requirements and call for a full mobilization of industry resources in these particular directions. The program adopted by this Division for dealing with the situation therefore becomes of special interest.

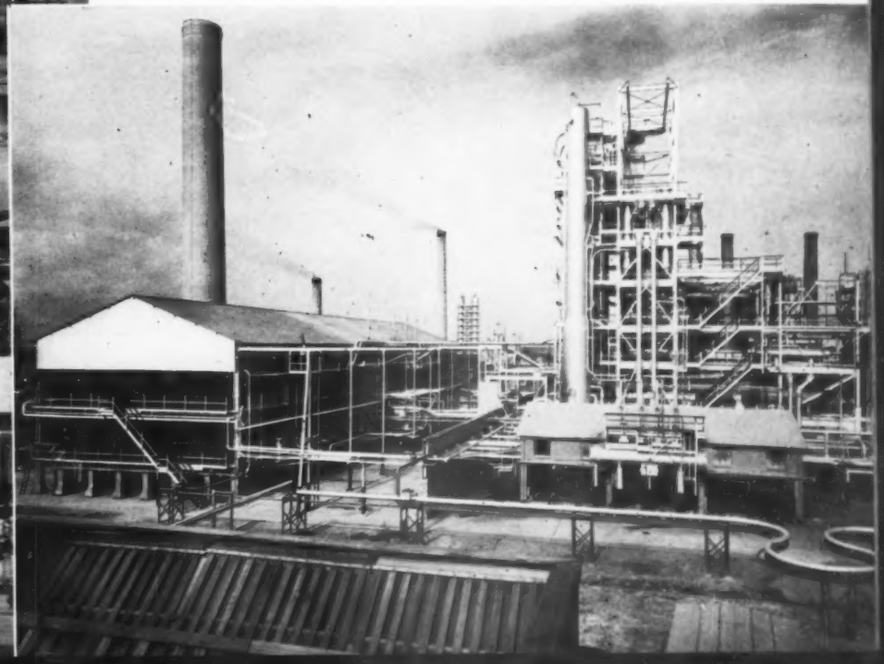
Work of the Division of Refining, as outlined to WORLD PETROLEUM by Director Wright W. Gary, is directed to coordinating the activities of the refining industry and assisting in satisfying its requirements along the following lines:

(1) Provision of materials necessary for effective functioning of the industry to meet increasing domestic and export demands.
(2) Increasing the production of aviation gasoline through existing and projected plants.
(3) Assisting in working out ways and means of financing and constructing additional plants for the production of 100 octane gasoline.
(4) Adjustment of specifications of refined products to provide maximum output and effectiveness of manufacturing establishments.
(5) Promoting the rapid and adequate distribution of refined products (in conjunction with the Division of Transportation).
(6) Handling of export orders and requests and survey of future export requirements.
(7) Establishment of priorities and arranging with the Office of Production Management for materials needed for maintenance and repairs; arranging with Army and Navy Munitions Board for new projects essential to defense; counsel with Joint Aeronautics Board and other departments on future requirements of the armed forces.
(8) General planning for provision of additional refining facilities.
(9) Adjusting inequalities and grievances of distressed refiners arising from emergency measures.

The above of course are only high points in the operating plans of the Division of Refining but they indicate some of the principal activities to which its attention is being directed. Two of the outstanding problems to the solution of which the Division of Refining is directing a considerable part of its energies at the present time are those of priorities and of increased production of 100 octane gasoline. The matter of priorities is one that has become increasingly troublesome to equipment manufacturers in the past few months as accumulating orders for the Army, Navy and lease-lend programs have absorbed more and more of available shop capacity. In the earlier period of the defense campaign the issuance of A-1-A ratings or defense preference requests by different departments and bureaus in Washington led to considerable confusion. In some manufacturing establishments these "must" contracts exceeded working capacity with the result that only in cases where direct representatives of the contracting authorities were posted in a plant, as is the practice of the Army and Navy, was prompt delivery obtainable while other orders with high preference ratings were unavoidably held up to the detriment of the defense effort.

In an effort to insure a more orderly handling of essential materials the Director of Priorities of the Office of Production Management on September 9 announced the adoption of a temporary plan establishing a preference rating of A-10 for maintenance and repair materials in twenty specified industries among which petroleum production, refining and transportation were included. This ruling was intended to avoid the delays involved in having each order follow its individual course through the government departments concerned, with the checking and investigation required in each case. Under its terms qualified producers and suppliers were permitted to apply the specified rating to deliveries of materials by endorsing on the purchase order the statement, "Purchase order for repair or



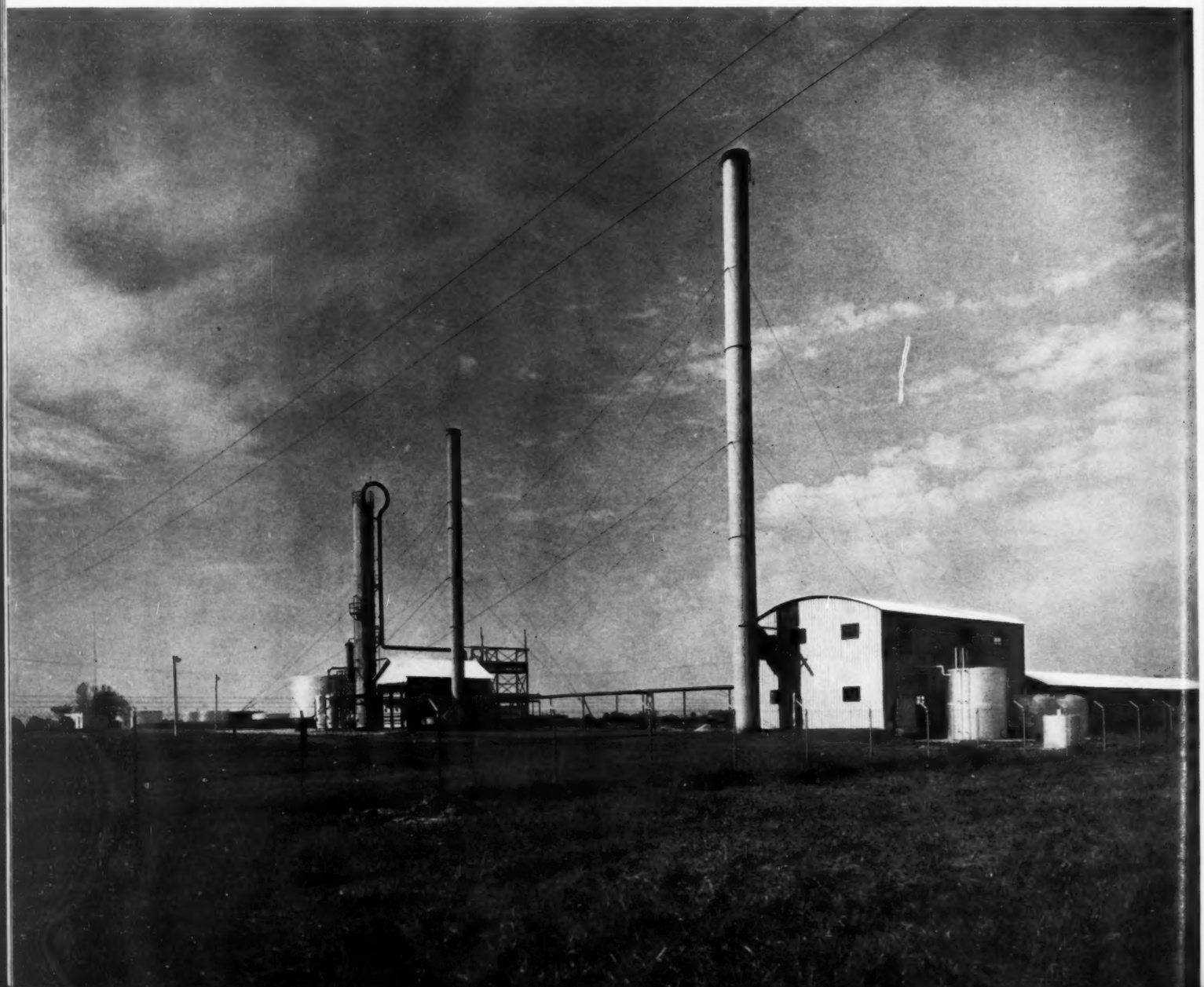


Left, unit for combined topping and cracking at an important Pacific Coast refinery; and below, Magnolia Petroleum Company's 10,000 bbl. per day polyform plant designed by Lummus for the production of 88 Research gasoline.

emergency inventory. Preference rating A-10 under Preference Rating Order P-22." This order, it will be observed, was designated as being temporary only. Its purpose was to tide over the situation until a more complete system of handling the whole vexing subject of adjustment between available supplies and imperative demands could be worked out. It was limited, however, to repairs and emergency inventories. Projects involving new construction still required special departmental action and issuance of "PD" orders entitling them to higher preference. Under the special ruling referred to a number of applications for refinery equipment were handled with greater dispatch than formerly. Many oil companies apparently assumed however that membership in the group of twenty specified industries in itself assured preferential treatment and were subjected to delay through neglect of the necessary endorsement on their orders. Meanwhile a reorganization announced by the President has placed the whole industrial phase of defense operations under the direction of the Supply Priorities and Allocations Board (SPAB in Washington) of which the Office of Production Management is the most important division. Director of Priorities Donald M. Nelson has set about the task of putting the priority system on a practical basis by moving to ascertain the extent of available supplies and productive capacity in each essential industry. Based on this information allocations will determine to what extent a balance can be struck between supply and demand which in turn will indicate in what directions and to what degree restrictions on normal commercial production may need to be imposed. Cooperating in this study the Division of Refining of the Petroleum Coordinator's office through materials sub-committees of its regional committees has been engaged in determining the volume of maintenance materials used during the past year, quantities on hand and materials required for the coming year. In the report to be compiled from this data materials will be classified according to their character and the report when completed should give a clear picture of the maintenance needs of the industry for the coming year.

No other subject is receiving as much concentrated attention from the Division of Refining at the present time as that of enlarging the output of 100 octane gasoline. When the original defense program was initiated in the early months of 1940 one of the first recommendations of Dr. Robert E. Wilson who was then serving as petroleum advisor to the National Defense Council was a doubling of the output of aviation gasoline which at that time was about 20,000 bbl. daily. This increase was accomplished within the year by individual action of the oil companies but meanwhile demands for this particular product to strengthen the war efforts of Britain and Russia and to supply the growing needs of the United States forces have raised requirements to such an extent that the Petrole-

The first refinery in the State of Wisconsin recently completed for the Wisconsin Oil Refining Company near Sheboygan. The unit shown has a capacity of 6,000 bbl. per day, draws its crude from Southern Illinois with delivery by rail and distributes its products through Eastern Wisconsin and Northern Michigan.



um Coordinator asked first for a doubling and then a trebling of output. Director Gary described the situation before a recent gathering of oil men by saying:

"The tremendous present and indicated future needs for 100 octane number aviation gasoline point to a definite need for a large increase in our national productive capacity. The national defense program is rapidly gaining momentum and as planes are built fuel must be supplied to make them effective. The battle of democracy is being fought on many fronts and on all of these fronts 100 octane number gasoline must be made available. Substantially all of it must be supplied by our own refining industry. This requirement, if not met through an immediate and substantial construction program, will result in a dangerous depletion of our already dwindling stores of 100 octane gasoline."

Sub-committees of each of the five regional refining committees have been charged with the task of making a survey of their areas and of proposing ways and means of enlarging the production of 100 octane number gasoline. There are definite limitations upon the number of refineries that can be brought into this movement inasmuch as the products needed are derived from refinery gases and it is not practicable to install iso-octane units in plants of less than about 5,000 bbl. daily capacity. On the other hand it is desired to utilize the smaller refineries as fully as possible and processes developed within the past few years make it feasible to undertake the production of high test products in plants where it would have been out of the question previously. Several of the smaller refining companies already have announced plans for the installation of such units and others are expected to follow suit as soon as necessary arrangements can be made. In the aggregate the smaller refineries are capable of a substantial contribution to the supply of 100 octane gasoline. Most of the major companies now have in operation alkylation, isomerization or other units for the production of high test fuel and the capacity of many of these is to be enlarged. Without indulging in estimates as to the rapidity with which production of aviation fuel can be stepped up the feeling among those who are working on the subject is that the problem will be satisfactorily solved. Production of 100 octane gasoline involves some considerations that do not apply, not in equal measure at least, to products that normally are in more extensive use. It is a specialty, and for the present at least it is largely a wartime specialty. With the ending of hostilities consumption obviously will fall off sharply. Refiners cannot be expected to make the heavy investment required for its production without definite assurance of being able to recapture their outlay. One of the tasks of the Division of Refining is to work out with financial agencies of the government plans for extending financial assistance in the erection of plants where this is needed or otherwise assuring those who undertake their construction against loss. The question of priorities presents no particular difficulty in the case of these plants. Since their product falls directly into the class of munitions they are assured of the highest preferential rating.

Organization of Division of Refining

Office of Petroleum Coordinator

Harold L. Ickes - - - - - - Petroleum Coordinator
Ralph K. Davies - - - - - Deputy Coordinator
Wright W. Gary - - - - - - Director of Refining
P. M. Robinson - - - - - - Asst. Dir. of Refining
Robert B. Cragin - - - - - - Asst. Dir. of Refining
Vernon M. Balzer - - - - - Refining Materials Expert

Refining District Offices

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Production of aviation fuel bears a direct relation to other refining operations. "If we are to maintain our present and expanded aviation gasoline output," to quote again from Mr. Gary, "we must provide the means to keep our refineries running in order to supply the required raw materials for the manufacture of 100 octane number gasoline. Furthermore, over-all operations must be balanced for all refinery operations; hence the source of aviation fuel raw materials will be limited. It is therefore essential that all possible sources of supply be carefully canvassed." Incidentally it may be pointed out that the production of 120,000 bbl. of 100 octane gasoline daily which is the goal immediately in sight is based upon supplying domestic and export needs for the coming year only as nearly as these can be estimated in advance. Beyond 1942 the uncertainties are too great to permit intelligent planning. Moreover the program now under consideration will enlist the full energies of the construction branch of the industry as it can hardly be carried out in less than a year under the most favorable circumstances. The number of plants that will be built has not yet been decided and will depend upon individual capacities but if the plan to establish some of them in connection with some of the smaller refineries is followed the total is likely to run to 40 or 50 units and the cost to be $125,000,000 to $150,000,000 or possibly more.

Many and varied technical problems enter into the work of the Division of Refining. Building up the production of 100 octane gasoline is the big job of the moment but tied in with this is the necessity of maintaining a balanced output of all refined products, of keeping the wheels of millions of indispensable motor vehicles rolling, of keeping homes heated and industrial plants in operation. The country's refineries are now operating at the highest rate in their history. Daily runs are around 4,000,000 bbl. which is close to the capacity of 4,181,000 bbl. reported for active plants on January 1 by the Bureau of Mines with 141,000 bbl. additional then under construction. With rising domestic and export demands not only for ordinary gasoline but also for distillate and residual fuel oil, lubricants and base stocks for high test aviation fuel provision of added refining capacity must be kept steadily in view. These are but a few of the many questions with which the Division of Refining is called upon to deal day by day. The problems are being attacked systematically and methods of solving them are being worked out through the active cooperation of the district committees and sub-committees. The team work that is being done by the representatives of the industry and of government provides a sound assurance of successful contribution to national defense.

Houdry Process Occupies Important Place in

NATIONAL DEFENSE

1,000,000 Bbl. of Houdry Aviation Gasoline Already Produced from Plants That Can Manufacture Ordinary Motor Fuel Without Costly Readjustments After Present Emergency is Ended.

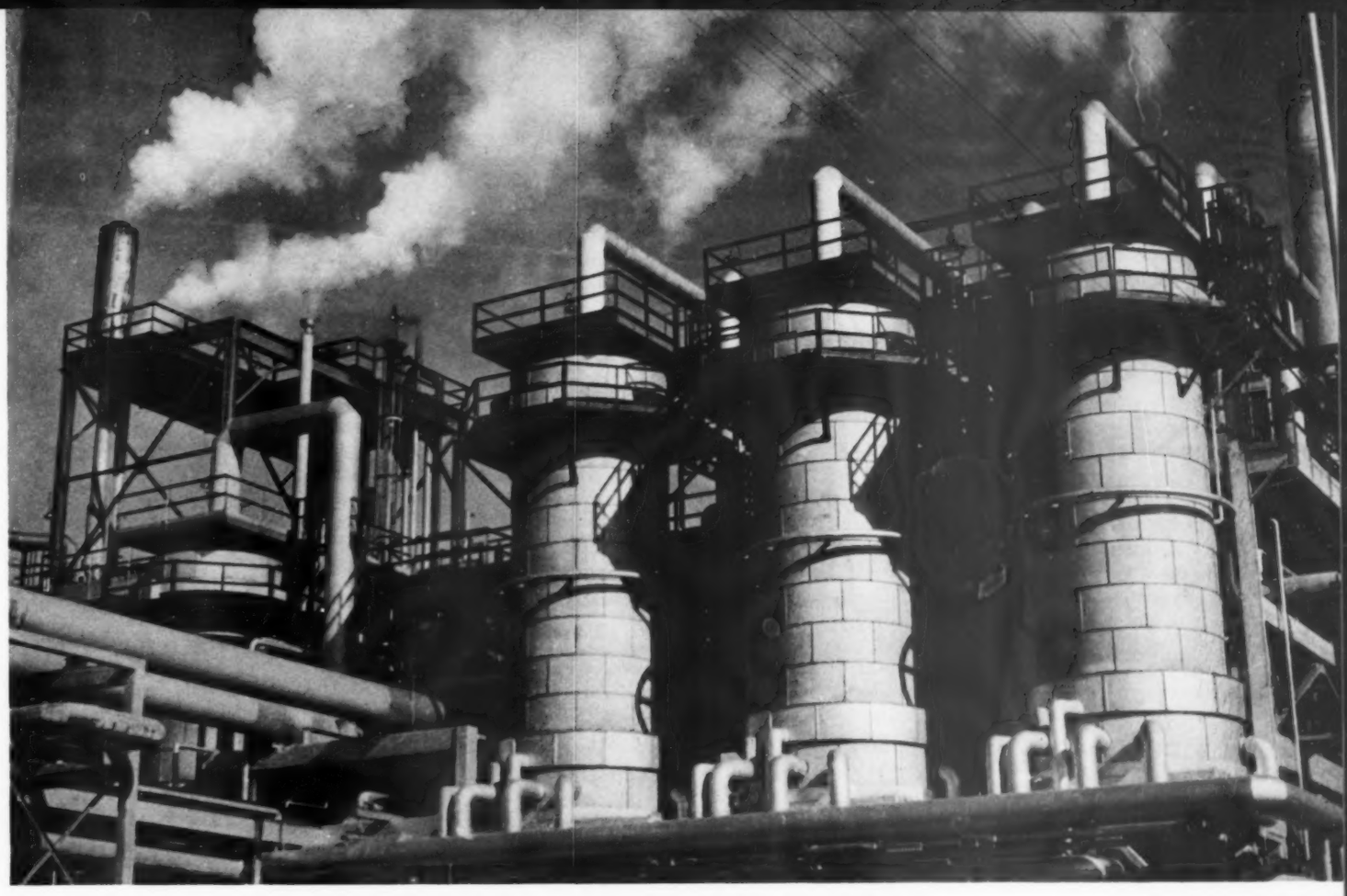
THE Houdry Process stands today as the sole catalytic cracking process which has a proven operating background and a demonstrated ability to produce commercially high octane aviation fuel and motor gasoline. The purpose of this article is to outline the development of the process, its present status and possibilities for providing fuel for our national defense effort. It will be realized that many technical aspects and developments cannot be fully discussed due to the present government policy regarding disclosure of technical information.

Today there are operating and under contsruction 16 Houdry Units, having a combined catalytic cracking capacity of over 200,000 bbl. and representing an investment of the order of $50,-000,000. These plants are producing aviation base and motor gasolines having a knock rating within the range of 78-81 A.S.T.M. octane and with a research octane on the motor gasoline of usually 87-90. The aviation fuel contains a high percentage of iso-pentane and other iso-paraffins in the light ends and aromatics and naphthenes as the higher boiling fractions. The fixed gas is rich in iso-butane and will also supply a portion of the butenes required for an alkylation unit feed stock. The catalytic gas oil produced can be recycled for the production of additional motor fuel or thermally cracked. Recovery and utilization of heat generated in the process has been improved to the point that for most units the utility consumption is only fuel and water and frequently there is an excess production of high pressure steam and electric power. The process today has far advanced from the original work done by Eugene Houdry in 1926 when he discovered that certain natural clay catalysts would produce high grade gasoline from Venezuela residuum. After confirmation of this phenomena there came the problem of revivifying the poisoned catalyst for further catalytic action. This was the major problem and successful utilization of the reaction depended upon its solution. Early work established that the yield decreased as the oil volume catalyst volume ratio increased, and therefore optimum yields would be possible only by bringing large volumes of catalyst in contact with the vapors. The possibility of doing this by continuously injecting the catalyst in the vapor stream, separation, and regeneration, was tried but due to the mechanical effort involved in moving the catalyst and difficulties due to its abrasive nature this method was considered inferior to regeneration in place and the shifting of the hydrocarbon vapor and the air regeneration medium as is done at present.

The first attempt at the regeneration of the catalyst ended in the disaster that has greeted many other experimenters. The heat of oxidation of the catalyst deposit was so great, and the thermal conductivity of the catalyst so poor that the result was a masse of fused catalyst and steel. Eventually the catalyst was successfully regenerated by circulating small amounts of fresh air with larger volumes of flue gas, the oxygen content of the incoming mixture being held so low that the heat of regeneration could be removed as sensible heat in the regeneration gases.

Obviously this procedure was slow. The problem was very much the same as that encountered in the burning of filter clays except the permissible loss of catalyst activity was much less. The amount of fresh air that could be admitted had to be kept very low in order to prevent the catalyst temperature from reaching the cintering stage, and the amount of flue gas recirculated had to be very high in order to remove as much heat as possible. In order to obtain a balanced cycle with one case on stream and only one or two in regeneration, it was necessary to keep a single catalyst case on a stream for a great number of hours. Since the catalyst loses activity with increasing time on stream as catalyst deposit is laid down, it is obvious that only very low yields could be obtained from this type of operation. The first improvement in catalyst case design was the incorporation of perforated tubes in the catalyst bed. These tubes conducted air and oil into all parts of the catalyst bed, and reaction products and regeneration gases from all parts of the catalyst bed, so that essentially all of the catalyst was being used or regenerated at the same time. These tubes, because of their considerable mass and heat content, also tended to reduce the maximum catalyst temperature attained during a regeneration. Within a short time, fins were welded onto the tubes, so as to assist in the temperature control of the catalyst mass. This procedure shortened the on stream period to the order of eight to twelve hours, but it was still necessary to depend upon the sensible heat of the regenerating media to carry away the heat of regeneration. The next step in the development of the catalyst container was in the use of a separate cooling medium to remove heat of regeneration. Numerous materials were tried, and water under pressure was used for a time. Present plants operate using a eutectic mixture of molten salts which circulates at all times through pipes in the catalyst mass. The pipes through which the salt flows are finned with steel plates of special design so as to remove readily heat from or supply heat to all sections of the catalyst. The cooling medium is cooled by exchange outside of the cases, and heat removal is so efficient that the on stream periods of individual cases in most modern plants is only ten minutes. It can readily be appreciated that with this short on

Houdry laboratory at Linwood, Pennsylvania, where research directed toward the discovery of more efficient catalysts is constantly in progress.



The impressive catalysts cases of one of numerous Houdry gas oil cracking units.

stream period, the catalyst is used at its peak of activity before an amount of catalyst deposit sufficient to poison seriously the cracking ability of the catalyst can be laid down.

Hand in hand with the development of the catalyst container were developments in other engineering phases of the process. When it became evident that heat of regeneration could be removed by a separate cooling medium, the question of optimum utilization of this heat became of prime importance. Under present design of Houdry cases and auxiliary equipment, the heat of regeneration is utilized in two major ways: first, as preheat by exchange to the oil feed; and, second, in the manufacture of high pressure steam. The utilization of regeneration heat to preheat crude by exchange results in considerable economies, particularly in combination units where the heat recoverable by this and other means may be sufficient to top the crude. Only reduced crude need then be fired, in a single heater. Because the heat of regeneration is recovered at a high temperature level, 800-850 deg. F., the manufacture of 475 lbs. steam by exchange is an easy task. The 475 lbs. steam is used in gas recovery plant reboilers and in turbines for pump drives. In the latter case, this steam is usually bled off at 150 lbs. for further process or pump use or other use.

About the time that the use of a heat exchange medium for regeneration temperature control was being developed, consideration was also being given to the use of air at higher than atmospheric pressure for the regeneration. There are several advantages to using air at higher pressures. Because of higher concentration of air in the catalyst chamber, greater burning efficiency is obtained on the oxygen of the air, and less air need be pumped to effect removal of a given amount of catalyst deposit. Moreover, the pressure drop occasioned by blowing air at atmospheric pressure is much greater than the pressure drop at higher pressure, and necessary air pipe sizes decrease inversely with the absolute pressure. By the use of a turbo-compressor unit, fresh air is compressed to the desired pressure by energy obtained by bleeding hot regeneration gases through a turbine. Due to the heat picked up by the air during regeneration, and also to the increase in volume due to formation of water vapor and CO, there is usually an excess rather than a consumption of power by this operation. This is usually recovered as electric power by means of a generator connected with the turbine. Further power may be obtained if desired by passing some of the 475 lb. steam generated through a steam turbine connected with the generator. This steam may also be bled off at 150 lbs. if desired. Many units now in operation and design so balance their power load that there is an excess rather than a consumption of steam and electric power, and the only net consumption of utilities is fuel and cooling water. Improvements in engineering design of catalyst cases and auxiliary equipment are being progressively made. As an example, a radically different type of case design, employing a new type of cooling medium, is now ready for commercial test. If proven successful on that scale, it will, according to preliminary economic estimates, effect additional reductions in plant investment and operating costs.

When the first satisfactory case was evolved, long before the present design was adopted, experiments were begun on catalyst improvement. First attempts were in the direction of improveing naturally occurring clays. Clays from many different sources were tested, with and without chemical and physical treatment, and certain clays and certain treatments were found superior to others. Various catalyst treating methods were developed, particularly treatments to adapt catalysts to the proper activity for different types of charging stocks, and have contributed greatly to the dependability of results obtained in commercial units. Nevertheless, although source of clay, chemical composition, physical properties, processing procedure, etc., were all held as constant as practical, the inherent catalytic properties of natural clays varied from shipment to shipment and this variation could not be entirely eliminated by any treatment developed. Because of this variation in the quality of clays, and to improve on the best clays available, work was

started on the manufacture of synthetic catalysts from chemical raw materials. Starting with chemicals containing the basic elements in natural clays, a seemingly infinite number of combinations of chemical composition and reaction procedure were tried. Other elements were added to and substituted for the elements in the clays. The effect of such variables as source of chemical raw materials, conditions of precipitation of the catalyst, concentration, pH, method of drying and molding all had to be determined. Once a catalyst was made in a reproducible manner which showed promise on one charge stock it had to be tried on charge stocks of widely different properties. It was also necessary to know whether a catalyst would withstand repeated regenerations, and this involved long and tedious catalyst ageing tests. After four to five years of study and development of the type outlined above, a plant for the commercial manufacture of one of the synthetic catalysts was erected. This catalyst is now being used in four operating Houdry units and is being prepared for replacement of clays in others. The synthetic catalyst now in manufacture is not considered by its developers to be the answer to all catalyst problems. For most services it is superior to catalysts made from natural clays. It gives higher octane gasoline than clay, and makes possible direct production of low acid heat aviation gasoline of high quality. With certain charge stocks, a reduction in catalyst deposit of 50 percent is obtained; on others the reduction is much smaller. Obviously, the minimum catalyst deposit possible is desired for a given yield of gasoline, since removal of the catalyst deposit is perhaps the major engineering problem in a catalytic plant. Needless to say, work is continuing on other catalysts at all times in the Houdry laboratories.

Largely due to the development of newer catalyst, it has recently become practical to recycle the catalytic gas oil back through a Houdry unit. Incremental increases in motor gasoline yield have been obtained on all recycle ratios tried, and the recycling procedure involves no increase in catalyst capacity or in equipment auxiliary to the reactor vessels. This feature would indicate further confirmation of the original decision to use a fixed catalyst rather than a moving catalyst operation. Yields up to 70 percent motor gasoline based on the fresh charge have been obtained by this type of operation, and the gas oil remaining is of approximately the same characteristics as that obtained with once-through operation. With once-through operations, yields are largely a function of installed catalyst capacity. With recycling, yields become a function not only of the installed catalyst capacity, but also of the recycle ratio used. With the advent of economic recycling with a Houdry unit, a tool of great flexibility is in the hands of the refiner. It is no longer necessary to depend upon conventional thermal equipment, producing low octane gasoline, for the processing of the catalytic gas oil to supply sufficient overall motor gasoline yield. In the instance of a refiner who has existing thermal capacity in good condition, the preferable installation may be a once-through Houdry unit, with heater and distillation additions for recycling as the thermal units fail or become inoperable as the most economical installation.

Table 1 gives yield and inspection data from representative Houdry recycling operations. The gasoline yields given range from 49 to 65 percent of the case charge. As is evident from this, recycling operations are not always run for maximum gasoline yield, but for incremental gasoline yield, with a given catalyst capacity, over once-through operation. The data of Table 1 represents incremental yields over once-through operations of nine to 19 percent. Attention is called to the high research octanes of the gasoline and to the quality of the catalytic gas oil.

FIGURE 1

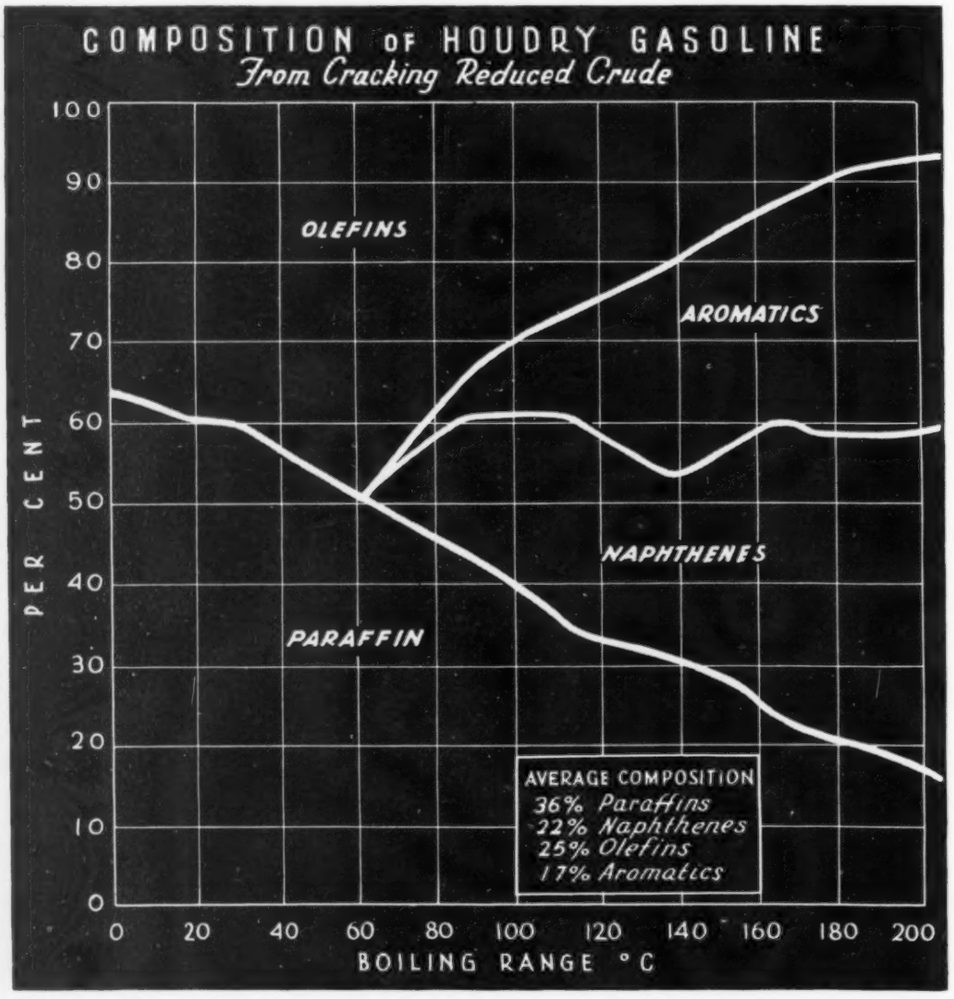


TABLE 1

Representative Yields From Houdry Recycle Cracking

Charge To Plant	East Venezuela Resid. and Gulf Coast Pressure Still Stock.	Reduced Mid-Continent Crude Plus Refinery Slop Oils	Mid-Continent Reduced Crude (54.9% B.t.ms.)	East Texas Gas Oil
Gr. deg. A.P.I.	19.4	25.8	27.3	35.9
I.B.P. deg.F.	...	500	440	432
10% deg. F.	631	583	490	488
50% deg. F.	898	810	700	540
90% deg. F.	...	...	...	642
E.P. deg. F.	...	...	...	718
Gr. deg. A.P.I.	7.7	17.4	16.9	...
Sulphur, %	1.58	0.35	0.51	0.19
Tar— % vol. of chg. to plant	35.7	38.4	34.1	...
Gr. deg. A.P.I.	7.7	17.4	16.9	...
Fresh Charge to Cases % vol. of chg. to plant	64.3	61.6	65.9	100.0
Gr. % A.P.I.	26.8	31.7	33.2	35.9
Dry Gas,, % wt. of fresh chg. to Catalyst	12.4	14.3	9.2	14.6
Catalyst Deposit, % wt. of fresh chg. to Catalyst	6.7	7.1	3.2	5.4
Gasoline, % vol. of fresh chg. to Catalyst	60.0	56.1	49.4	65.5
Gr. deg. A.P.I.	58.7	58.8	58.5	56.0
50% deg. F.	247	231	232	380
50% deg. F.	247	231	232	210
90% deg. F.	370	365	376	380
R.V.P. p.s.i.	9.3	10.0	10.0	9.5
Sulphur, %	0.13	0.01	0.03	0.02
C.F.R.M. octane number	80.0	79.6	79.0	78.2
C.F.R.M. octane number	92.1	89.1	89.0	88.0
Catalytic Gas Oil, % vol. of fresh chg. to Catalyst	30.1	29.6	44.1	21.3
Gr. deg. A.P.I.	21.9	26.9	31.0	34.3
10% deg. F.	539	488	481	486
50% deg. F.	625	556	536	518
Pour Point deg. F.	64	...	...	20
Viscosity, S.S.U. at 100 deg. F.	49	40	39	36
Aniline Point, deg. F.	141	...	145	148

Gasoline produced by a Houdry unit is uniformly of 78 to 81 C.F.R.M. octane, regardless of the crude source of the charge stock. C.F.R. Research octane varies over the wider range of 85 to 95. Gasoline from a recycling operation may be a point higher in motor octane than that from once-through operation, and the research octane is generally about two-points higher. The work of the Cooperative Fuel Research Committee which was reported at the May, 1941, meeting of the American Petroleum Institute has pointed out the importance of compounds other than paraffins in modern motor gasoline. The road test work there reported shows that the octane demand of 90 percent of the engines tested decreased from 78.5 at 750 R.P.M. (15 m.p.h.) to 66 at 3000 R.P.M. (60 m.p.m.). A sample of Houdry gasoline, made on old type catalyst, of 76.5 C.F.R.M. octane, was found under the same conditions of test, in an equally large number of cars, to perform as 83 octane at 750 R.P.M. as 70 octane at 3000 R.P.M. and to have the same octane-engine speed slope as 95 to 100 percent of the cars tested. This gasoline, which appears almost exactly to match the requirements of a modern automobile engine, had the analysis shown in Figure 1, and is typical of the gasoline which would be produced from the once-through processing of a reduced crude. Eighty-five to ninety-five percent of the paraffins are iso-paraffins, and it is evident that the octane in the front end of the gasoline is due to its high iso-paraffin content. The octane of the heavier end of the gasoline is due to the larger quantities of aromatics and naphthenes present. Figure 2 shows the analysis of a sample of motor gasoline obtained by once-through Houdry cracking of East Texas gas oil. A comparison of the two charts will disclose the primary difference between once-through Houdry gasoline produced from gas oils or lighter stocks and from reduced crudes or heavier stocks. The gasoline from the light stocks, due to the catalysts and operating conditions employed, contain practically no olefins. This means that, since the A.S.T.M. octane is unaffected (79-80) and aviation gasoline equal to or better than the best straight run gasolines can be produced. Furthermore, because of the high isopentane content of Houdry gasolines, it is unnecessary for the refiner to purchase or manufacture additional iso-pentane for vapor pressure and octane improvement.

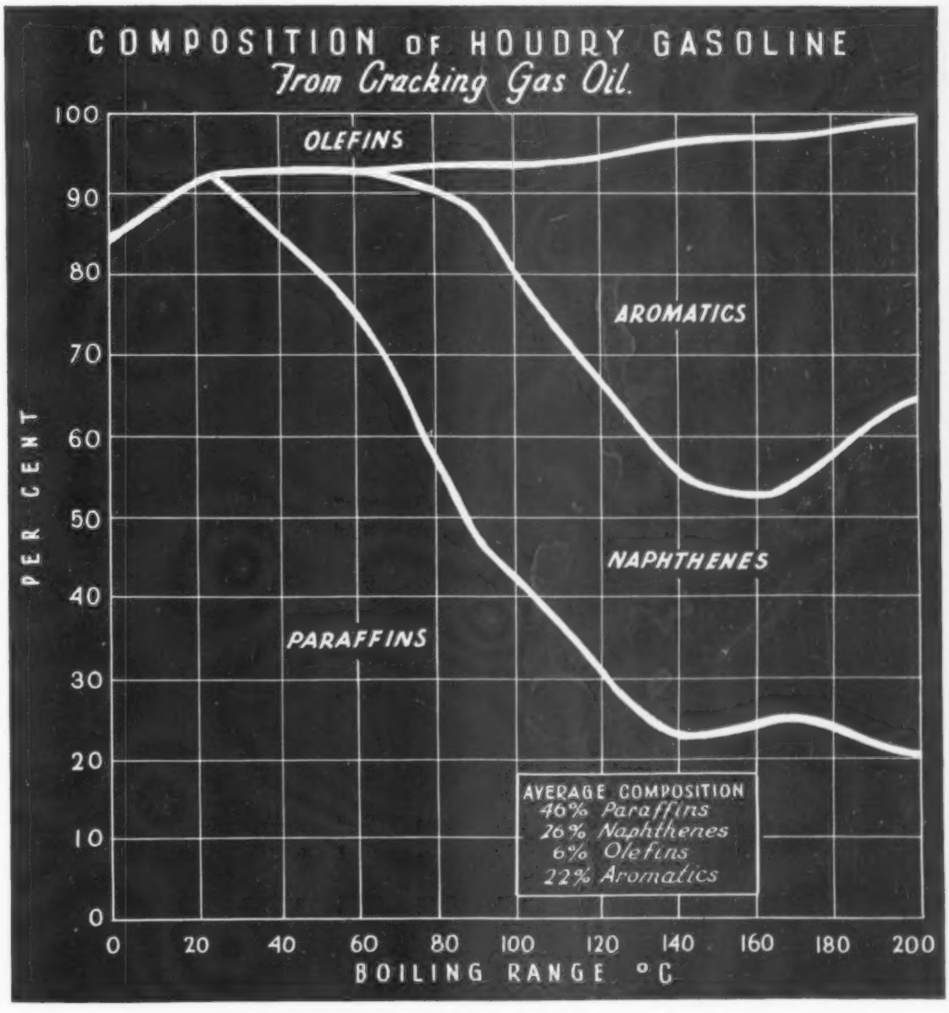
Aviation gasoline produced by the Houdry processing of naphthas and gas oils will be of 20 to 40 acid heat, and when blended with alkylate to produce 100 octane gasoline the acid heat will be correspondingly lower. With 3cc T.E.L. per gal, the octane of the Houdry aviation base will range from 91 to 94, and 100 octane gasoline can be produced by blending with an average of 40 percent of hydro-codimer or alkylate plus 3cc T.E.L. This alkylate requirement will be seen to be considerably less than that required with most straight run gasolines, and it should be particularly noted that no outside iso-pentane is necessary. The vapor pressure of debutanized Houdry aviation base gasoline will range from seven to eight pounds Reid, and this is due to its high isopentane content. The data in Table 2 give representative yields from once-through processing of two representative gas oils and naphthas. It can readily be seen that the source of the crude has practically no effect upon the quality of the aviation gasoline produced. In connection with the production of aviation gasoline, preliminary studies of a simple treating method have indicated that the already excellent lead susceptibility can be improved and that with 4cc T.E.L. AFD-1C octanes of the order of 96 to 99 can be obtained without the use of high octane blending mediums such as hydrocodimers or alkylates. Attention is called to analyses of the gases (total C_4 and lighter) shown in Table 2. Approximately 40 percent by volume, or almost 55 percent by weight, of the gas made is iso-butane. This is sufficient to supply a major portion of the iso-butane necessary to provide alkylate to bring the Houdry aviation base to 100 octane with 3cc T.E.L. If desired, by a change in operating conditions, the gas make can be increased at the expense of only the cycle stock, to the point where the iso-butane output of the Houdry unit is sufficient to provide all of the iso-butane needed for the alkylation unit. At this time, the butenes produced will be approximately one quarter of those required for the alkylate.

TABLE 2

Data From Once-Through Houdry Cracking of Gas Oils and Napthas

Charge to Catalyst	Grade B Coastal Gas Oil	East Texas Gas Oil	Grade B Coastal Heavy Naphtha	East Texas Naphtha
% volume of crude	39.8	25.5	24.9	21.2
A.P.I. gravity, deg.	31.9	36.1	38.5	42.3
Initial boiling point, deg. F.	484	440	356	348
10% point, deg. F.	529	474	372	366
50% point, deg. F.	576	535	418	411
90% point, deg. F.	680	660	468	480
End point, deg. F.	712	728	491	514
Aniline point, deg. F.	161	166	...	...
Sulfur content, %	0.21	0.03	0.03	0.03
Yield Data				
Excess Iso Pentane, % vol. of chg to Case	3.0	2.4	1.7	1.9
Aviation Gasoline 7 lb. R.V.P., % vol. of chg. to case	37.0	33.0	26.8	22.8
Avia. gaso. base for blending, % vol.				

FIGURE 2



chg.	40.0	35.4	28.5	24.7
Avia. gaso., 160 octane - base + iso octane — % vol. charge	66.7	61.0	47.5	46.6
Motor, naphtha, % vol. of chg. to case	7.4	11.4	33.3	36.2
Catalytic gas oil % vol. of chg. to case	41.1	37.5	30.2	28.5
Dry gas from avia. gaso., % wt. of chg to case	12.4	14.6	9.3	10.5
Catalyst deposit, % wt. of chg. to case	5.4	5.1	1.8	1.9
Motor gasoline, % vol. of chg. to case	48.8	49.3	66.7	66.6
Dry gas from motor gaso., % wt. of chg. to case	10.8	12.7	5.9	6.3
Inspection of Products				
Aviation gasoline				
A.P.I. gravity, deg.	65.1	63.7	61.3	61.2
10% evap. at deg. F.	138	135	138	136
50% evap. at deg. F.	193	191	207	201
90% evap. at deg. F.	275	275	281	294
Reid vapor pressure at 100 deg. F. p.s.i.	6.8	7.0	6.9	7.0
Sulfur, %	0.01	0.01	0.01	0.01
Acid heat, deg. F.	27	27	27	27
Copper dish. corrosion	O.K.	O.K.	O.K.	O.K.
Copper dish. gum. MG. per 100 ML.	3	1	2	1
Oxygen bomb. induction period, hours	10+	10+	6	6
U. S. Navy Accelerated Gum	4.6	3.1	20 (3.1 with 5 lb. alpha naphthol/ 1000 bbls. gasoline)	23.5 (5.5 with 8 lb. alpha naphthol/ 1000 bbls. gasoline)
Freezing point deg. F.	←76	←76	76	76
Freezing point deg. F.	←76	←76	76	76

Heat of combustion B.t.u. per pound (net or low. val.)	19,202	18,686		
CFRM-ASTM octane.	78.7	78.6	79.2	77.9
Octane AFD-1C after addition of 3 ML. per gal. T.E.L.	93.0	91.5	94.0	93
Octane T.E.L. 4 ML.	94.5	93.5	94.7	94
Motor Naphtha				
API gravity, deg.	36.1	36.1	40.8	
CFRM - ASTM octane number	80.5	77.1	58.9	
Sulfur, %	0.01	0.01	0.01	
Catalytic Gas Oil				
API gravity, deg.	26.8	32.3	33.6	40.6
% point, deg. F.	480	448	440	363
50% point, deg. F.	528	500	460	400
90% point, deg. F.	624	594	513	478
End point, deg. F.	724	690	631	516
Aniline point, deg. F.	111	136		130
Sulfur, %	0.15	0.14		0.01
S.U. Vis. at 100 deg. F.	36	34		31
Motor Gasoline				
API gravity, deg.	54.9	59.3	54.4	53.3
10% evap. at deg. F.	129	126	158	150
50% evap. at deg. F.	231	219	158	150
90% evap. at deg. F.	346	356	389	389
Sulfur, %	0.02	0.01	0.01	0.01
Reid vapor pressure at 100 deg. F. p.s.i.	10	10	10	10
CFRM - ASTM octane				
CFRM-ASTM octane after addition of 1 ML. per gal. T.E.L.	85.2	85.8	78.9	69.5
CFRM - ASTM octane after addition of 3 ML. per gal. T.E.L.	90.0	90.1	83.2	77.5
Dry Gas from Aviation Gasoline				
Hydrogen MO 1%	4.5	4.5	2.3	7.1
Methane MO 1%	10.1	11.1	7.2	10.8
Ethene-Ethane MO 1%	6.6	9.0	5.5	7.6
Propene MO 1%	7.1	10.4	16.4	11.2
Propane MO 1%	10.2	16.5	8.8	15.6
Isobutane MO 1%	41.7	37.6	40.9	29.9
Isobutene MO 1%	1.09	1.5	3.4	2.3
N-butene MO 1%	9.8	6.2	8.3	7.6
N-butane MO 1%	8.2	3.2	7.2	7.9

NOTE: 95 AFD-1C Octane hydro-codimer used for 100 octane blends.

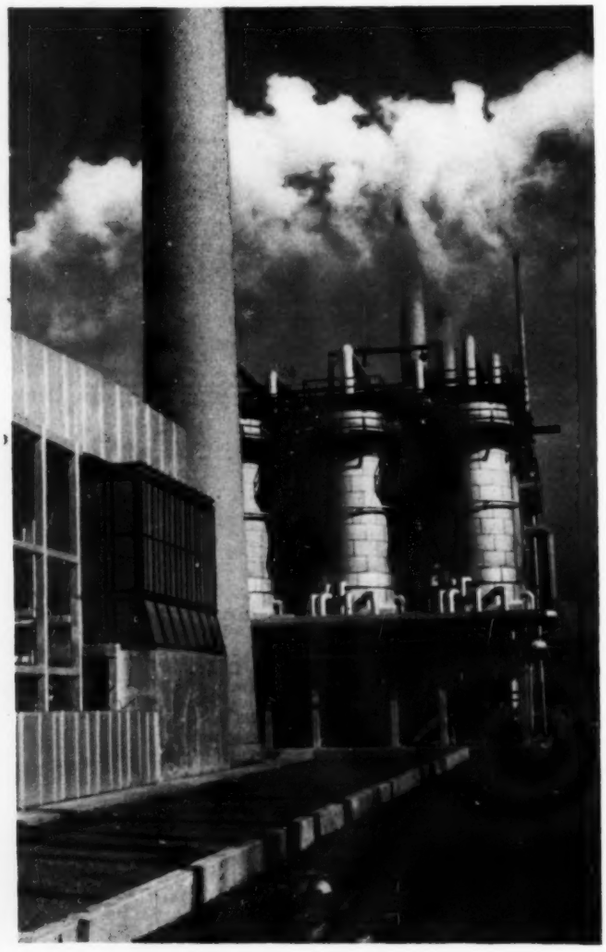
In the past five years over a million barrels of Houdry aviation gasoline have been manufactured and sold. This gasoline has been used by the United States Army and Navy and the commercial air lines. There is no question about its performance. The accompanying table 3 gives analyses of Houdry aviation base gasolines from representative sources before blending with alkylate. For some time back it has been felt that saturated hydro-carbons were the only ones desired in high grade aviation gasoline. Opinion is changing, however, and it is now felt that moderate amounts of aromatics are not only beneficial but necessary for the best performance under all flying conditions.

TABLE 3

Composition of 7 lbs. RVP Aviation Gasoline, approx. 280 deg. F. at 90%

Charge Stock	Vol. % of Gasoline			
	Olefine	Aromatics	Naphthenes	Paraffines
Gas Oil from Grade B Coastal Crude	9.1	11.7	21.6	57.6
Heavy Naphtha from Grade B Coast. Crude	6.0	16.0	25.0	53.0
Gas Oil from E. T. Crude	7.7	16.3	18.4	57.6
Heavy Naphtha from E. Texas Crude	10.0	17.3	23.4	49.3
Range	6-10	12-17	19-25	50-57

A corner of the heater may be seen against the background of catalyst cases at a Houdry cracking unit.



From the foregoing, the place of Houdry catalytic cracking units in the defense organization of the country is evident. With a given alkylate production, from 33 to 50 percent more 100 octane gasoline can be produced, and no iso-pentane need be purchased or manufactured by costly installations. When the present emergency is over, alkylation units and isopentane superfractionators will probably be of limited use. Houdry units will continue to be operated economically for the production of high grade motor gasoline. If it is desired to operate the Houdry unit on heavier charge stocks, such as reduced crudes, a change of catalyst may be necessary, depending upon the specific case, but no costly equipment changes will be needed to convert the installation.

Under present operations, the Houdry aviation gasoline cut can be blended to 100 octane gasoline, sold alone or with straight run as 91 octane gasoline, or if these markets are at any time insufficient to use the entire unit output, may be blended into motor gasoline production. The heavy naphtha from gas oil operations will be 79-80 octane, and may be blended into motor gasoline. Excess butane production will provide a vapor pressure lift for the naphtha.

62 Million Gallons of Toluene Yearly For NATIONAL DEFENSE

By O. W. Willcox

Oil Industry Plans to Furnish Explosive Sufficient for 4600 Rounds of 16-Inch Rifle Ammunition Per Day From Toluene Units.

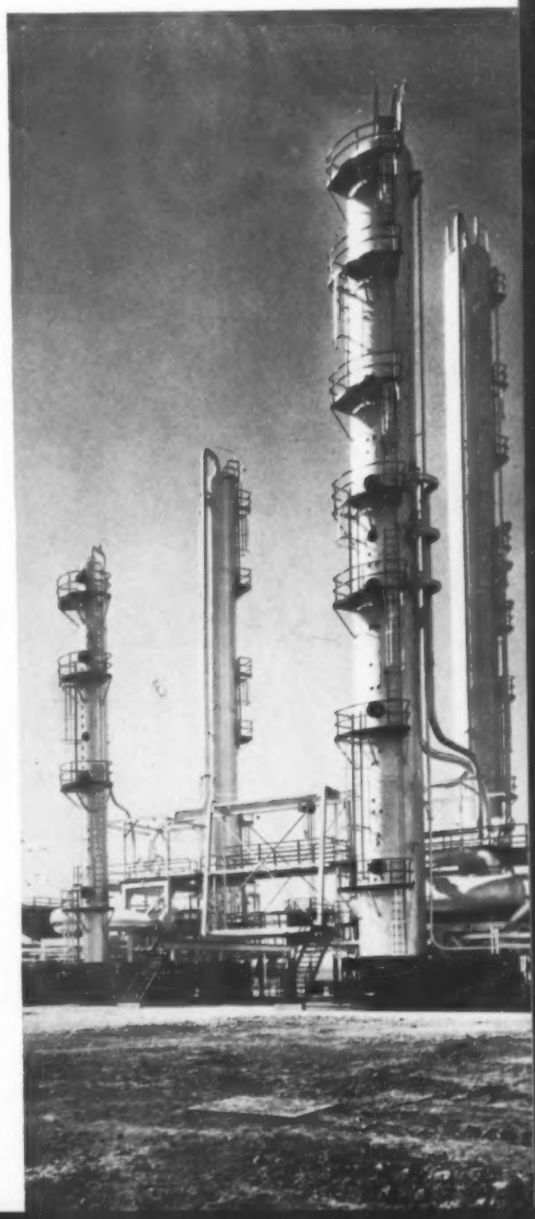
ASIDE from reconnaisance, for aerial transport of parachutists, and for fighting other planes in the air, the chief function of a military airplane is to drop bombs on ships, land fortifications, and industrial plants. Merely for flying through the air a bomber or other airplane is wholly dependent on aviation gasoline, a petroleum product. The bombs that the plane drops are charged with trinitrotoluene, which is made from toluene, now also a petroleum product. In a double sense, therefore, the petroleum industry is a vital source for the materials of aerial warfare which is proving itself decisive today.

It has been estimated that the defense program of the United States should provide for an annual supply of 500,000,000 to 600,000,000 lbs. of trinitrotoluene in order to be sure of having enough for a full-scale war effort. This will mean that there must be produced, somehow, about 50,000,000 to 60,000,000 gallons of toluene a year. Where is this toluene to come from? The chief source of toluene up to the beginning of the present emergency has been the coal tar which is obtained as a by-product in the dry distillation of coal, such as occurs in the operation of coke ovens and gas manufacturing plants. In 1939 the amount of toluene produced in the United States from this source was about 20,000,000 gallons, or about a third of the estimated military need, but nearly all of this peacetime production was being absorbed by civilian industry for the manufacture of solvents for paints and for other solvent purposes, and for the manufacture of dyestuffs and many other indispensable materials. To commandeer these 20,000,000 gallons of toluene for exclusively military purposes would result in much inconvenience, and even then to depend on existing sources would create a bottleneck. It has therefore become necessary to tap other sources of supply, the chief of which is petroleum.

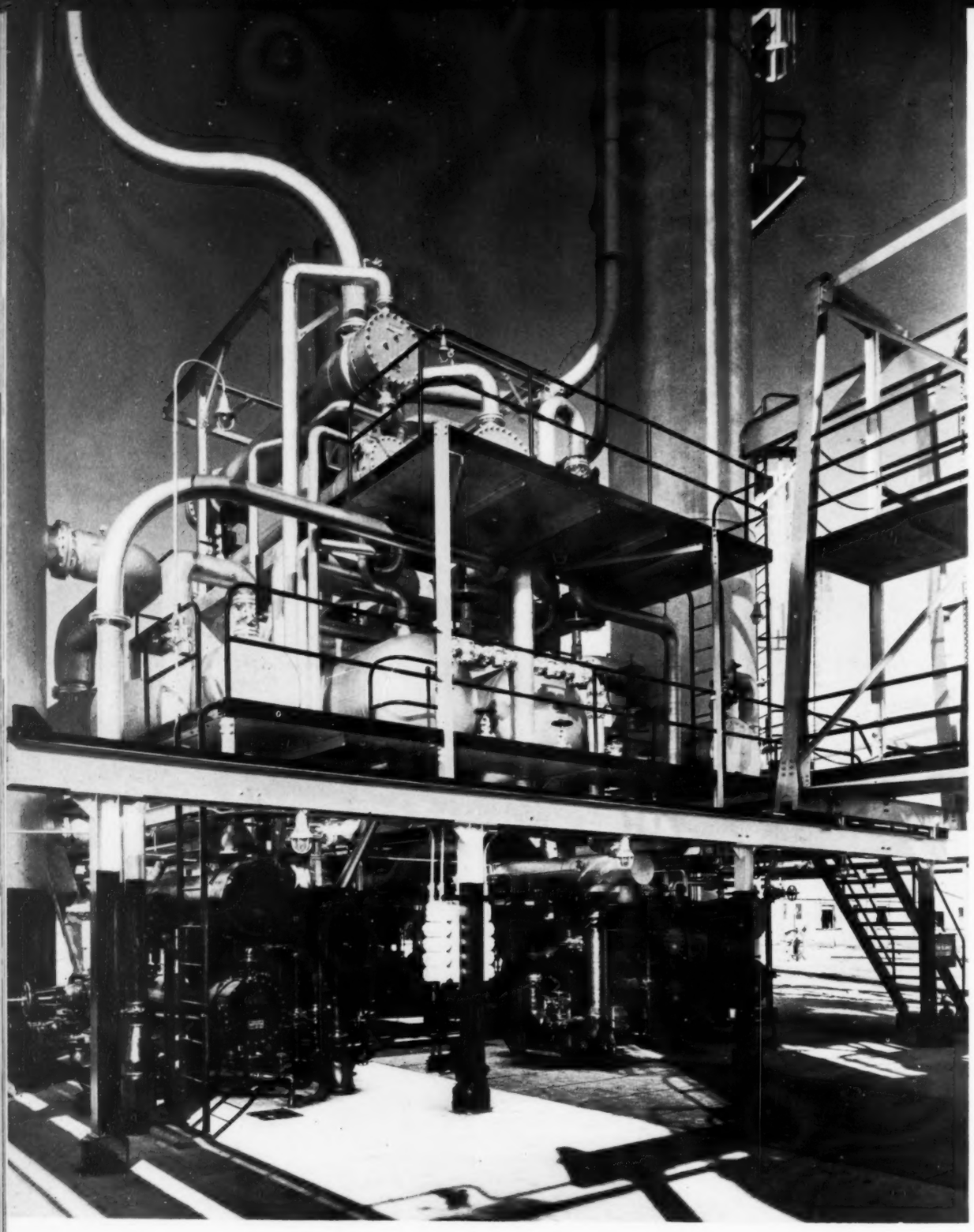
Many crude petroleums contain small amounts of toluene and other hydrocarbons of the aromatic series, particularly after passing through the usual cracking operation. To separate the toluene from crude or cracked oil, requires a more or less simple fractionation. Several refineries have for some years been accustomed to recover commercial amounts of distillates rich in toluene for sale to paint and varnish makers. However, such fractions are not sufficiently pure for military purposes. The statement that the separation of toluene from crude or cracked oil requires a more or less simple fractionation needs a little clarification. In the case of a crude oil straight run distillate little contaminated with olefines or naphthenes, only a straight fractionation is required, so that where the toluene content is even as little as 0.4 percent of the charge it may be recovered. Cracked distillates on the other hand contain ten times as much toluene, but from cracked distillates the separation of this large quantity is a complicated process, due to the very complex character of the cracked product. Some of the cracked substances form azeotropic mixtures with toluene that cannot be broken up by fractional distillation and this makes it necessary to resort to various devices, among which are included treatment with selective solvents.

Up to date, the Shell Oil Company has taken the principal lead in the separation of military toluene by fractional distillation. The first such plant was completed in December, 1940 at Shell's Deer Park refinery, Houston, and placed in operation to produce 2,000,000 gallons of toluene a year. In May, 1941 the Shell Company contracted with C. F. Braun Company for the erection of a duplicate of this plant to cost approximately $1,000,000. This will raise the toluene output of the Deer Park refinery to 4,000,000 gallons a year. In August of this year Shell also contracted for the erection of a third toluene plant, this time at its Wood River refinery in Illinois, which will have an annual capacity of 4,000,000 gallons of toluene, and will bring the total toluene capacity of the Shell Oil Company up to 8,000,000 gallons a year. It has been stated that if similar equipment were installed at all of Shell's other refineries, the total annual output of toluene by this company would reach 40,000,000 gallons.

At the same time the problem of toluene supply is being attacked on a larger scale in another quarter. In this case a richer supply of material for fractionating is being utilized. Except in some natural foreign crudes, such as those of Borneo and Roumania, which for obvious reasons do not come into consideration for the purposes of American defense, the amount of toluene in most natural crudes and in crudes that are cracked by ordinary methods is small, seldom reaching or exceeding 10 percent, and thus requires the handling of large volumes of distillates in order to obtain quantity production. In some of the newer cracking and reforming processes the amount of toluene found in the cracked or reformed gasoline is much larger, and can be made quite large by controlling the process so as to make the production of toluene and other aromatic hydrocarbons the main instead of the secondary product of the operation. Such is the case with the recently perfected hydroforming process which is being licensed by the M. W.



Fractionating equipment in Shell's recently completed toluene unit at the Deer Park refinery in Houston.



Heat exchangers, accumulators and equipment for separation of toluene by fractional distillation. This Shell Company unit at Houston can produce 2,000,000 gallons of toluene a year. A duplicate of this plant will soon be in operation at Deer Park.

Kellogg Company. This process was primarily designed for and is still mostly used in the manufacture of high octane base blending stocks for aviation gasoline. This process employs a catalytic reaction which in chemical terms is a combination of hydrogenation, dehydrogenation, and aromatization. The preferred raw material is a straight-run heavy naphtha. This material is heated and mixed with gas rich in hydrogen recycled from a previous operation. This mixture passes through a reaction vessel charged with a special catalyst material, and issues as a product from which is obtained a yield of 80 percent of an 80 octane A.S.T.M. gasoline. The interesting point in this connection is that the high octane number of this gasoline is due in no small part to the formation of large amounts—up to 50 percent or more of aromatics, principally toluene and xylene, of which 15 to 20 percent is toluene. By appropriate modification of the process, instead of merely producing a high octane blending gasoline base, the aromatics content of the product can be raised to 80 percent with a proportionate increase in the yield of toluene. This synthetic process seems well adapted to meet the demand for military toluene, once the plants already built, building or planned, come into full production.

The first of these hydroforming plants to come into consideration as a producer of toluene is the Texas City refinery of the Pan American Petroleum and Transport Company, which was started up late in 1940. This plant is designed to process 7,500 bbl. a day of straight run heavy (uncracked) naphtha of 40-45 octane number,

which would normally be converted into 80 octane gasoline. When operated for toluene the annual output of this product will be equivalent to 5,000,000 gallons. The second hydroforming plant to be constructed with an eye to the production of military toluene is a new 4000 bbl. a day unit of the Continental Oil Company at Ponca City. This plant will be in a position to turn out about 2,500,000 gallons of nitration-grade toluene a year. In addition to these facilities is a large unit which has just been put in operation by the Humble Oil and Refining Company at its Baytown, Texas, refinery. This unit is designed for hydroforming a charge of heavy naphtha amounting to 16,000 bbl. a day. The total cost of this unit with its accessory equipment is stated to be $11,860,000. The government furnished the money and owns the plant, which will be operated by Humble Oil and Refining Company on a cost-plus basis. It is expected that the output of toluene from this unit will be in excess of 10,000,000 gallons a year, which it is said might eventually be raised to nearly 27,000,000 gallons by the operation of auxiliary units that may soon be installed.

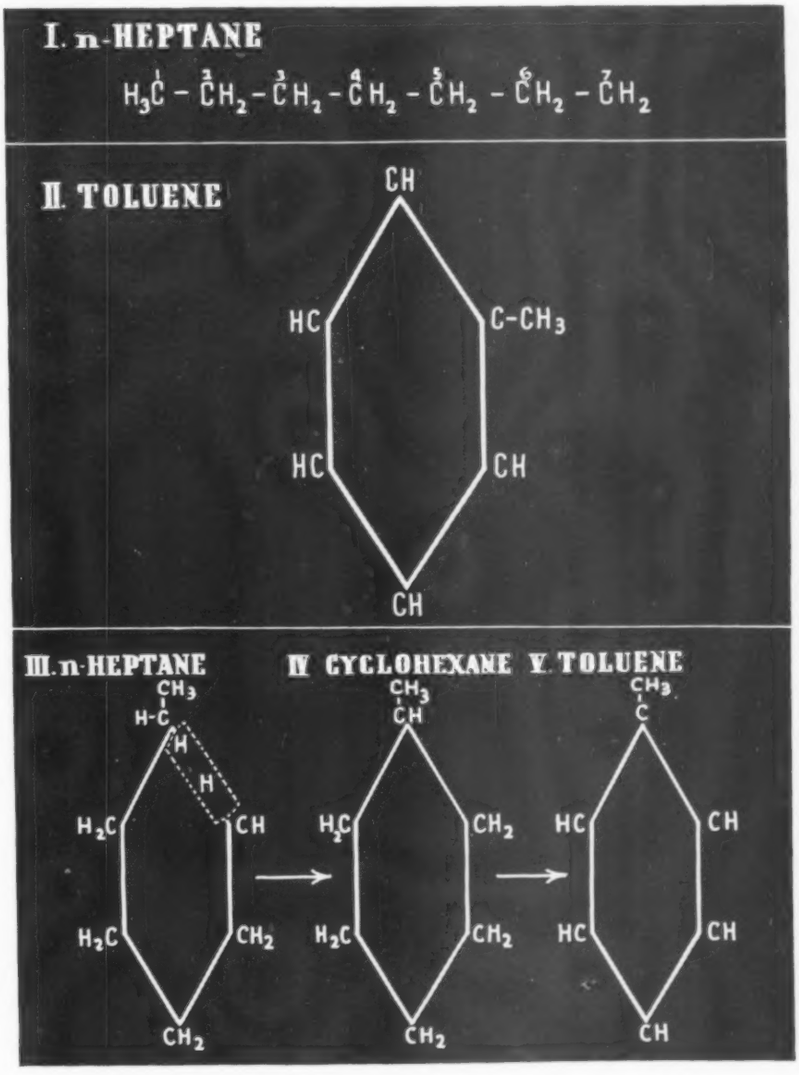
The whole of the above mentioned facilities sum up to a total of about 42,500,000 gallons of military toluene a year. This could be further increased by pressing into service two other hydroforming units that are being planned without reference to toluene production.

If the military authorities have not understated their requirements, it appears that the toluene situation will hardly become a bottleneck in the war that has now come very close to the Americas. This is quite different from the case in World War 1, when the coke and the gas works were the only available commercial sources of toluene in the United States, and they were then producing far less than the 20,000,000 gallons produced in 1939. It was known in a limited way that toluene was present in small quantities in cracked petroleum, but the conditions under which it was formed were unknown. Nevertheless, the problem was attacked energetically, if somewhat blindly. It was learned that the most suitable charging material was a distillate stock, and a plant was erected by the General Petroleum Corp. at Vernon, California. Without much theory or practice as a guide, a cracking operation was hit upon that enabled this plant to turn out about 200,000 gallons a month. Meanwhile erection of a similar plant was started by the Standard Oil Company of California at Richmond, but the end of the war put a stop to such operations. The difference between the old and the new situations lies in a better understanding of the transformation of paraffin hydrocarbons into aromatic hydrocarbons, and particularly in the discovery of catalyst materials that make it easy to effect this transformation.

The paraffin hydrocarbon most suitable for conversion into toluene is normal heptane, generally written n-heptane, although higher members of the series which can be broken down into n-heptane also come into consideration. N-heptane and its higher homologs are plentiful in the upper gasoline distillation range and in naphthas. Hence, such distillates are good charging stocks for toluene manufacture. Why n-heptane lends itself to this synthesis will be clear from the accompanying diagrams. (I) represents the normal heptane molecule. It is a chain of seven carbon atoms (C); the two end atoms carry three hydrogen atoms (H_3) and the middle ones two hydrogen atoms (H_2). (II) represents the toluene molecule. It is a closed ring of six carbon atoms, with the seventh carbon atom and its three hydrogens (CH_3) hanging on one side; the other six carbon atoms in the ring are reduced to one H atom each.

Inspection of (I) and (II) will suggest that if a normal heptane molecule is looped on itself and the first carbon atom (No. 1) tied to No. 6, and the hydrogen atoms on the ring carbons reduced to one each, the result would be a molecule of toluene. This is exactly what happens when distillates rich in heptane or heptane-yielding straight chain hydrocarbons are passed over a chromium oxide catatyst in the hydroforming process. The various stages in this transformation are indicated by diagrams III, IV and V: III shows an atom of hydrogen being removed from each of carbon atoms 1 and 6 so that a ring may be formed. The result is the ring compound IV, which is cyclohexane. Then in a further phase of the process one hydrogen is removed from each of the ring carbons, giving V, which is toluene.

Some authorities have lately insisted that instead of figuring on 60,000,000 gallons of toluene a year the army and navy should ask for 100,000,000 gallons, and others have multiplied this by three. If the higher estimates prevail, the oil industry could still comply, but it will have to be given much assistance and considerable time.



Distillate Production For Direct Utilization

Distillate production from pressure maintenance plants contributes a small but important output to the total refining capacity which has lately become of critical importance.

While Small in Volume Distillate Production Has Valuable Characteristics Requiring Minimum Treatment to Make it Available as Motor Fuel—May Help to Relieve Possible Strain on Refining and Transportation Facilities During Emergency.

Ulric Meisel

DISTILLATE PRODUCTION

WHEN the first gas well was drilled in the Agua Dulce field in South Texas over a decade ago and when a gas well was completed by a major oil unit on the Stratton structure nearby several years later, the owners considered their discoveries essentially as failures. As a matter of fact, those companies disposed of most of their properties consisting of thousands of acres because at that time they saw no value in a gas field in this area. Fields closer to population and industrial centers assured a long-time supply from those fields and as a consequence the more distant fields had to wait for a market and exploitation. Such projects represented unsatisfactory investments for oil companies which had to look to income in the more immediate future. These two discoveries represented types of gas reservoirs of which there were presently to be a considerable number. An earlier gas field of this character was the Big Lake 1929 discovery, although the older Big Lake dark oil producing horizon overlain by a gas-distillate gas sand, was discovered earlier and was producing in 1929.

A gas-distillate well is considered as a gas well except that before the fall of 1932, the production from the Big Lake gas sands, produced with an outstandingly low gas-oil ratio, was considered as oil, white oil to be sure, but oil nevertheless. A condensate or distillate well was earlier considered to produce a water white or nearly water white product of relatively high A.P.I. gravity at a high gas liquid ratio. In the fall of that year Dr. Wm. N. Lacey, in a discussion before the California Institute of Technology of an A.P.I. paper delivered by E. V. Foran, suggested the theory that the white oil produced in the traps in this field was the product of condensation outside the reservoir and the oil or condensate was in the vapor phase in the reservoir. In spite of the attention which this discussion received at the November meeting of the A.P.I. in 1932, this "oil" continued to be produced as crude oil, and the "casinghead" gas produced concomitant therewith was processed in a conventional gasoline plant to be treated as natural gasoline.

Wet gas with substantially lower liquid content was generally recognized as gas, and production of the gas for the small gasoline content

Ulric Meisel

was not permitted in Texas under laws enacted as early as 1925, and confirmed by the courts in Henderson versus Railroad Commission of Texas, 1932, unless a legal use was made of the remaining gas after separation of its liquid content. Owners of substantial wet gas reserves were impelled to defer the recovery of gasoline or naphtha for economic reasons as well as by the restraints of conservation laws. They desired to recover the liquid content but did not want to destroy the latent value of the gas reserves for their future value as fuel and for the possibilities of using the gas as raw chemical material in the production of fuel and plastics. Polymerization was in its infancy and great promise was held out that a large part of United States' supplies of motor fuel would ultimately come from this source. Plastics originating with ethylene from butane had passed the laboratory stage.

Some owners or lessees of properties of this character recovered what they could of the heavier components of this type of gas in field separators operating at relatively low pressure, but wasted the gas into the atmosphere for as long a time as they could avoid impact with the regulatory bodies. In several cases, as at Big Lake and Agua Dulce, operators processed the separator gas through conventional absorption gasoline plants operated at pressures up to 300 lb. per sq. in., while in other cases operators limited their production of condensate to what they could recover from gas for which they had a market. But in the main, the increasing number of distillate reservoirs uncovered by the drill remained undeveloped or only partially developed, for want of an efficient and necessarily legal method of production or because there was a market only for a small fraction of the gas.

Presently a recovery method was to be found which met requirements of both efficiency and legality. As a result of research and experimentation conducted over a considerable period, a new operation was introduced which taught the feasibility of producing efficiently gas-distillate gas wells at high pressure combined with the return of the dry gas to the reservoir. One such plant, commonly called a recycling plant, went into commercial operation in the Agua Dulce field in January 1937. It embraced what has been referred to as a unitary process for distillate recovery consisting essentially of four major steps: (1) the delivery of gas to the plant at substantially well-head pressures; (2) the separation of the condensate at high pressure; (3) the compression of the residue gas, and (4) the reintroduction of the gas through properly located wells into the same reservoir, to maintain pressure therein for the purpose of preventing liquefaction by retrograde condensation, and to promote the travel of wet gas toward producing wells.

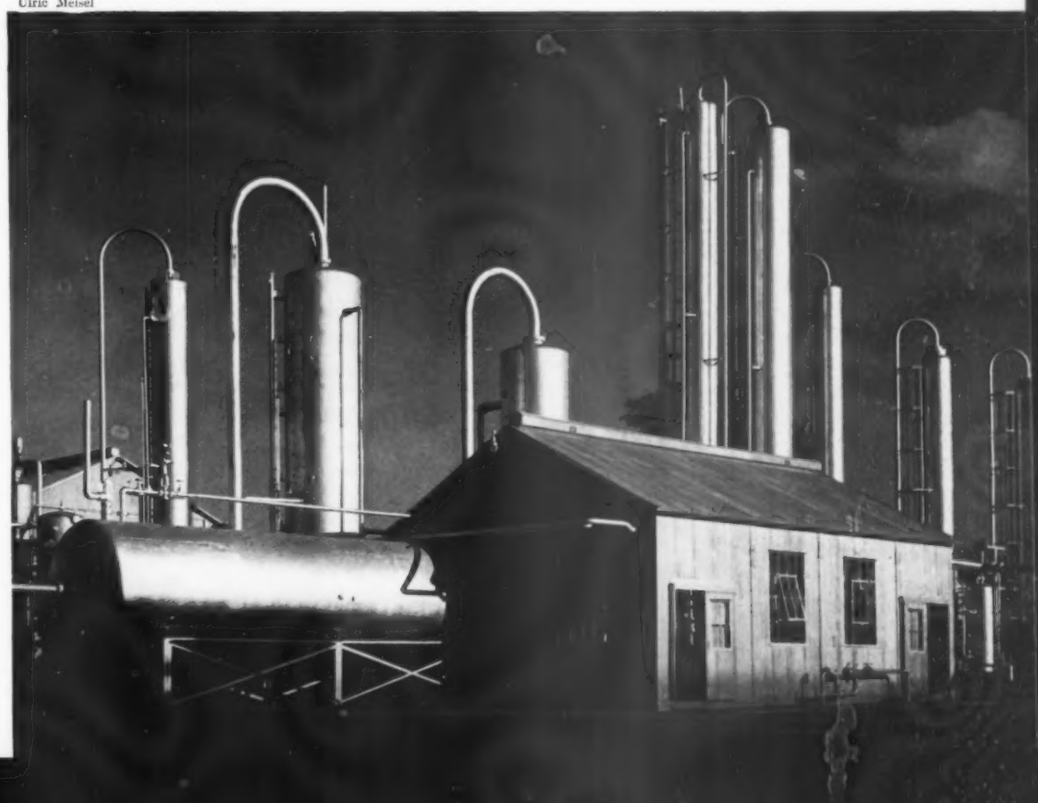
Cycling, or recycling as it is now commonly known, introduced a new phase in petroleum production practice. The method not only provides an efficient process for recovery of such liquefiable fractions as are contained in the gas produced, but equally important is the fact that only by returning the gas to maintain substantially virgin pressure in the reservoir is it possible to prevent liquefaction of substantial quantities of hydrocarbons in the reservoir from which they cannot be produced. As long as reservoir pressure is maintained, these fractions remain in the vapor phase until they are taken from the reservoir and removed from the gas stream This method of production assures maximum ultimate recovery. Extraction of the liquefiable fraction at high pressure provides high suction pressures to the compressors, so increasing their efficiency that the ratio of compression of the dry gas to the high pressures required to offset reservoir pressures has been reduced in typical cases to from five to one, or to put it another way, has reduced investment requirements for compression by 60 per cent. Whereas it was uneconomic to compress dry residue gas from plant extraction pressures of 30 lbs. or even 600 lbs. up to the 3000 lbs. required for cycling in specific instances, compression from 1,500 or 1,800 lbs. to the same pressure generally was within the economic range. This factor is more easily appreciated when it is pointed out that the compression facilities represent the largest single element of cost in a processing plant. There are situations where the gas is extremely rich in liquefiable content and where it would have been economic to compress the processed gas to the formation even from the relatively low pressures at which extraction plants operated in the days before the advent of cycling. Gas containing three and a half gallons of condensate could of course absorb two or three times the cost of compression involved in plants processing gas containing three quarters of a gallon or one gallon of condensate per thousand cubic feet of gas. Cotton Valley was such a field, but quite apart from other considerations, the operators did not cycle because such an operation was not envisaged during the immediate years following the discovery of the field. As a matter of fact, gas was produced at low pressure, the distillate separated, and the remaining gas sold or used as fuel. It was not until 1940 that all of the operators of this field came to recognize the importance of cycling dry gas back to the reservoir, and completed a plant for this purpose in the spring of 1941. However, it has been estimated that some 14,000,000 bbl. of distillate have been irrecoverably lost by condensation in the reservoir due to diminution in pressure below the dew point of those hydrocarbons of which the distillate is composed. It is this type of loss that cycling is designed to stop or greatly diminish, quite apart from the recovery effectuated on the surface.

The above ground operation of recycling operations vary from plant to plant in many respects. The plant of Tide Water Associated Oil Company and Seaboard Oil Company at Cayuga, Texas, operates at a pressure within a few hundred pounds of the static well-head pressure. In this plant the available pressure is maintained through the cooling exchange with water, gas exchange with the cold dry gas and cooling by contact with expanded ammonia gas, after which it is reduced to 1,200 lbs. Here the maximum normal and retrograde condensation is effected.

The circulation of brine in the wet gas stream prevents formation of gas hydrates and permits temperatures as low as 10 deg. F. In the plant of the same companies at Long Lake, substantially the same operation is employed except that

Recycling or pressure maintenance plants such as those shown below and on the facing page not only contribute to conservation in the production branch of the industry, but also add to the supply of refined products in a measure more important than is indicated by the quantitative figures.

Ulric Meisel



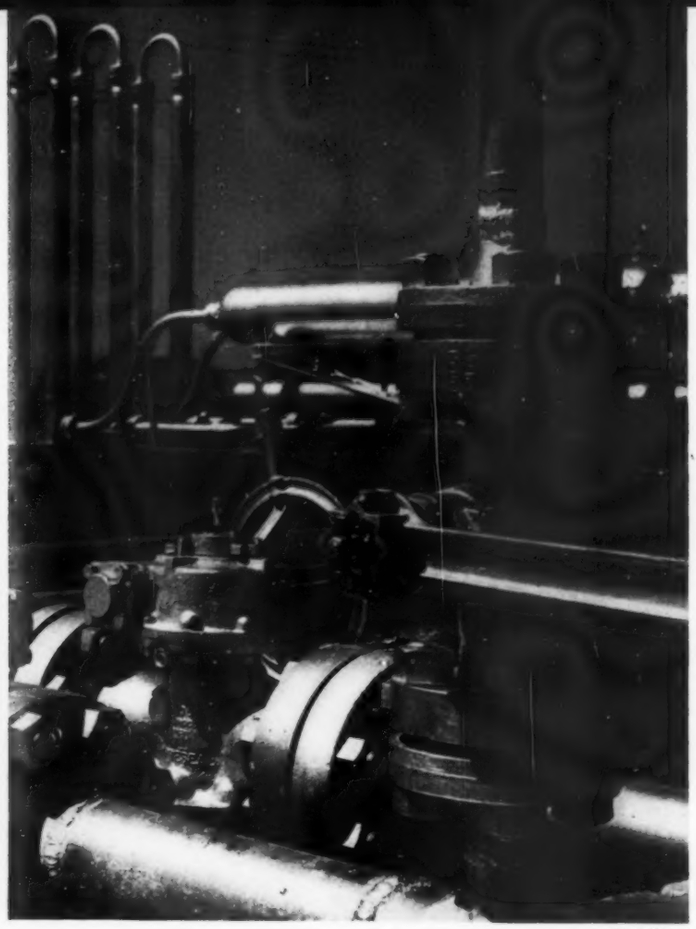
into the separator which has a number of bubble trays a narrow cut of distillate is introduced above the top tray. In this operation, a pressure of 1,500 lbs. was found to show satisfactory results. The first recycling plant to go into commercial operation, that of Process Oil Co., cooled the gas by water exchange, but it also introduced into the gas stream a quantity of precooled heavy condensate which not only cooled the incoming gas, but agglomerated the small particles of condensate and acted as an absorbing medium for the lighter components of the liquefiable vapors. Pressures upwards of 1,200 lbs. were maintained in the final separators. Later plants incorporating essentially this flow have operated efficiently at 1,850 lbs. In a large number of plants the gas is cooled by water exchange and the pressure dropped in a separator, the liquid removed, and the gas treated in an absorber at pressures maintained in the separator. A portion of the condensate is used as the absorbing medium. Plants employing this cycle are operating at pressures from a minimum of 1,000 lbs. to a maximum of 1,750 lbs.

So successful was this new method and so great the need therefore that in the intervening period of slightly more than three years since the first unit was installed, thirty-three complete plants have been put into operation and some ten are definitely planned or under construction. Already nearly 2,000,000,000 cu. ft. of gas is being processed daily in these plants and the residue gas returned to the reservoirs. This residue gas will be available, free of gasoline, as and when the need is developed for large volumes of gas to supply the ever increasing gargantuan requirements for industrial and civilian use in the larger centers of population. If the necessity for supplying this demand with respect to a given field should become imperative before all of the wet gas in the reservoir has been processed, very substantial irreplacable losses of condensate would occur. The greatly increased demand for gas, at this writing reported as running at 15 percent above 1940, particularly occasioned by the accelerated demand for power of all kinds in defense industries may, and doubtless will, result in new transportation systems, some going into the remotest sections of South Texas. As a matter of fact one of the largest projects of this character to be projected is in the process of development, and as far as can be ascertained, some gas-distillate gas reservoirs will be tapped for at least a part of the gas requirements.

Condensate production in point of volume alone is not sufficiently comprehensive to be of critical importance in the national petroleum supply at this time nor is it likely to become so in the immediate future. However, at present there is produced approximately 35,000 bbl. a day in plants along the Gulf Coast with some 15,000 bbl. in sight from proposed plants or facilities under construction, and an additional 15,000 bbl. daily from a rich distillate field in Kern County, California. Production of condensate or distillate not produced in plants, such as that at McKamie, Arkansas, is not included. While the volume of distillate or condensate production is not of major importance, at a time like this the production of every barrel of motor fuel which can be produced with a minimum taxing of other manufacturing facilities should be encouraged. As will be shown herein, distillate as produced in the cycling plant, may be converted into merchantable motor fuel without refining if desired, thus releasing these facilities or in any event avoiding the necessity for expanding them.

An interesting aspect of recycling is its relation to conservation, both direct and indirect. As is manifest from what has gone before, recycling is conservation *par excellence*. By recycling, the desirable liquefiable components of the gas may be efficiently recovered at the surface and the gas returned to the reservoir with 40 to 50 percent of the energy cost required at low pressure. Maintenance of pressure in the reservoir by the reintroduction of dry gas prevents condensation in the reservoir and insures maximum ultimate production of the condensables on the surface. Timely extraction of condensables will prevent the waste thereof if a critical demand develops for a fuel supply from a distillate reservoir before recycling has been completed. Maintenance of near virgin pressure assures saving of gas as such for future demand. The maintenance of pressure makes possible wide spacing of wells. With current stringencies in basic materials of all kinds, wells can be spaced even more widely than heretofore with no loss resulting therefrom. Large areas of gas sands may be drained by single wells. Spacings of one well to 160 acres up to 640 acres are not at all out of question where oil wells are drilled on 1/16 to 1/8 as much acreage. Moreover, the volume of condensate produced from each well can very well be from three times to ten times the production of an oil well over any sustained period of time without detriment to the well or the formation. Oil wells are in many instances cut back for want of a market or to protect the formation against rapid dissipation of the gas energy or too rapid encroachment of water, either of which would permanently affect ultimate production from the well. There is a large back-log of production due to proration, as stated, but in the past few months there has already been an increase of nearly 400,000 bbl. per day in output, chiefly from opening up some of the wells. It goes without saying, however, that while many wells can easily produce at a substantially higher rate without waste, others can produce more oil only at the cost of excessive energy loss. Wells over-produced now will mean ultimate loss in recovery from the structure. These losses will be felt, if not tomorrow, then in the future. But the losses will be felt and the future is not too distant. Condensate wells, on the other hand, are usually produced at very much less than one fourth of their open-flow capacity and never beyond that, but until there is a dilution by dry gas being returned to the formation, the liquefiable content of the gas, and hence the production from the well remains constant over any period of time. The volume of gas taken from a well is limited only by two considerations, (A) the differential pressures in the reservoir and (B) the content of the gas. If too great a volume is taken from a well there may be a pressure drop in the area around the well bore sufficient to cause some drop in content due to retrograde condensation. This is seldom experienced because wells are generally of large capacity and only a fraction of their output is taken to the plant each day for extraction of condensate.

At Cotton Valley alone the engineers of the operators reported that the recycling plant would save the drilling of 64 wells at $125,000, each, or $10,750,000 and would result in an ultimate increase in production in excess of 40 percent. On the other hand the Opelika and Katy fields in Texas, and Paloma in California doubtless have the same factors in savings, but all distillate reservoirs have substantial savings in proportion to these. The importance of recycling increases in significance when considered in the light of the foregoing. But if the supply of distillate is not of major importance in point of volume, its physical characteristics give it a value considerably in excess of its volume. For ready reference inspections of four typical distillates or condensates from as many fields are set down in Table 1. Note the refined character of all of the products regardless of the field from which they originated. These are natural products after stabilization only, yet they are sweet, noncorrosive and sulphur free.



Ulric Meisel

Details of the elaborate, high pressure piping in a Texas pressure maintenance plant. The products from a growing number of these plants have become increasingly important as blending agents for motor fuel.

TABLE 1

Characteristics of Typical Condensates

	1.	2.	3.	4.
Gravity	64.1	55.2	83.0	61.7
Doctor	Negative	Negative	Negative	Negative
Color	Water White	22	30	20
Odor	Sweet	Sweet	Sweet	Sweet
Sulphur, % ..	0.1	0.00	0.0	0.01
Copper Dish..	Negative	Negative	Negative	Negative
	Degrees Fahrenheit			
Boiling Point deg. F. ...	96	94	66	95
10 Percent	144	166	81	156
20 Percent	179	192	92	181
30 Percent	215	217	106	200
40 Percent	248	237	124	220
50 Percent	282	260	145	238
60 Percent	321	294	170	244
70 Percent	374	336	199	291
80 Percent	441	400	234	330
90 Percent	544	490	293	408
End Point	606	568	385	498
Recovery, Percent	94	97	95	96.5
Residue, Percent	3	1.5	1	1.5
Loss, Percent	3	1.5	4.0	2.0

It is readily apparent that the distillates shown contain from 75 to 100 percent of hydrocarbons boiling within the motor fuel range. The balance, with the exception of a few percent of bottoms of gas oil in several cases, is kerosene. The distillate may, of course, easily be distilled into these several products and it is in fact done at a number of cycling plants as a part of the recovery process. Quite apart from the ordinary economics of production costs considered from the standpoint of the proprietary operators of cycling plants, distillate or condensaate production takes on added significance when viewed as part of the national motor fuel situation. This is so for a number of reasons stemming from the component composition of the product.

(1) The product is so nearly entirely motor fuel that a minimum conversion cost is required to make it available as motor fuel or motor fuel base stock. (2) No chemical treating is required to sweeten the fuel or to make it meet severe corrosion tests, thus releasing treating chemicals such as caustic, litharge, copper salts, etc. for other uses. (3) The freedom of distillates from sulphur compounds makes them, like natural gasolines, highly responsive to tetraethyl lead so that less lead is required to build high octane into fuels which use distillate or condenstate as part of the base stock, again releasing for other uses lead and chlorine which are ordinarily required to refine or improve fuels produced from crude oil. To illustrate the high lead susceptibility of this type of gasoline sample inspections on several East Texas distillates are shown in Table 2.

(4) Perhaps the most important point in this connection is that the transportation of distillate by pipeline, tank car or tanker from the Gulf Coast to the Eastern Seaboard, or elsewhere for that matter, results in a high transport efficiency if considered in terms of the effective volume of gasoline delivered. Every barrel of distillate is the equivalent of one and a half to two barrels of crude oil, depending upon the grade of crude oil and the degree of refining to which that oil is subjected. The transportation of heavy fuels as part of crude oil is, of course, not an entire loss, but at this particular time emphasis must be laid upon motor fuel because substitution fuels, in which there is yet no transportation bottleneck, can be used for residual fuels at least until adequate Gulf Coast-Eastern Seaboard transportation facilities are again fully available. It is therefore a happy circumstance that distillate production has come at this particular time, and that it came at an apposite location readily accessible to pipeline and water transport.

The four small cycling plants operating in 1938 produced less than 1,000 bbl. of condensate or distillate a day. The product was not stabilized and was sold as produced to crude oil pipelines or processors. No effort was made to extract the lighter fraction or to save them. However, beginning in 1939 most of the existing plants, and plants which came into production in that year and since, borrowed a leaf from natural gasoline manufacturers. They not only added facilities to produce stabilized gas-free condensates and motor fuels, but in many cases provided process equipment to extract and segregate normal and isobutane, the latter for the increasing market provided by aviation gasoline manufacturers at prices which justified expenditures required for those facilities. In several of the larger cycling plants in excess of 10 percent of the total production is isobutane, nearly 2,000 bbl. per day being accounted for by two such plants.

The suggestion from the Oil Coordinator's office in late September that there be a 200 percent increase in the production of aviation gasoline of 100 octane, will find recycling and natural gasoline plants instantly responsive. For a variety of sound reasons producers of aviation base stocks, even where they are available in relatively large quantities at one location have not entered the ranks of aviation gasoline manufacturers and are apparently satisfied to serve as suppliers of those important raw materials. Nevertheless, as suppliers they are making important contributions to the national effort in providing this country with the extraordinary requirements for aviation and high octane gasolines, requirements greatly increased by the Lend-Lease operations and by the aid-to-Russia program upon which we are embarked. Recycling, along with its affiliated industry, natural gasoline, are playing their parts in the defense effort, quietly but effectively as well as contributing to conservation.

TABLE 2

	A	B	C	D
Vapor Pressure	9.4	7.65	8.0	6.5
Octane No. A.S.T.M. ..	58.0	55.2	56.6	54.1
CC Lead to 72 Octane ...	1.0	1.25	1.14	1.36

Tests conducted before new Research method was introduced

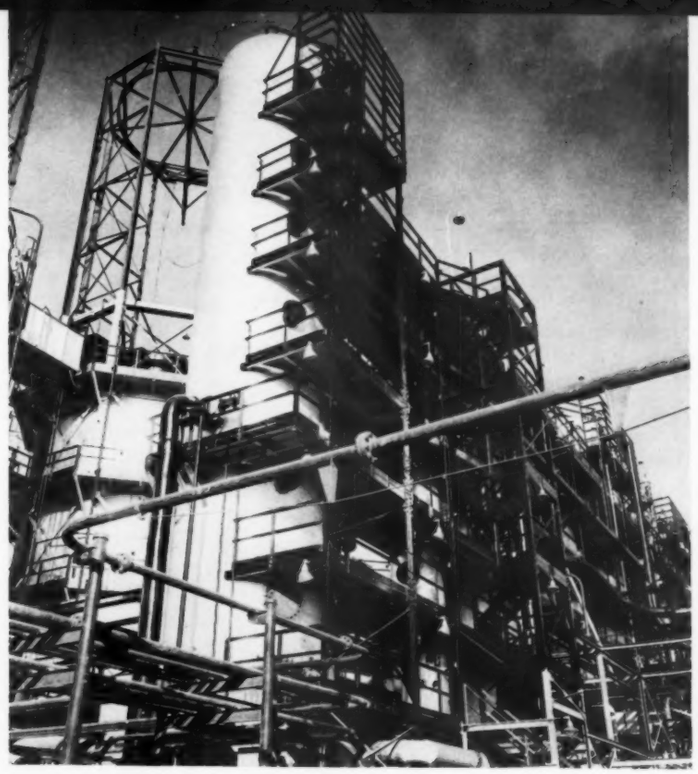
The United States leads the world in production of high octane gasoline at such plants as the Oleum Refinery of the Union Oil Company pictured directly above, the Watson Refinery of the Richfield Oil Company shown at the right above, and Gulf's aviation gasoline plant at Port Arthur, shown on the right.

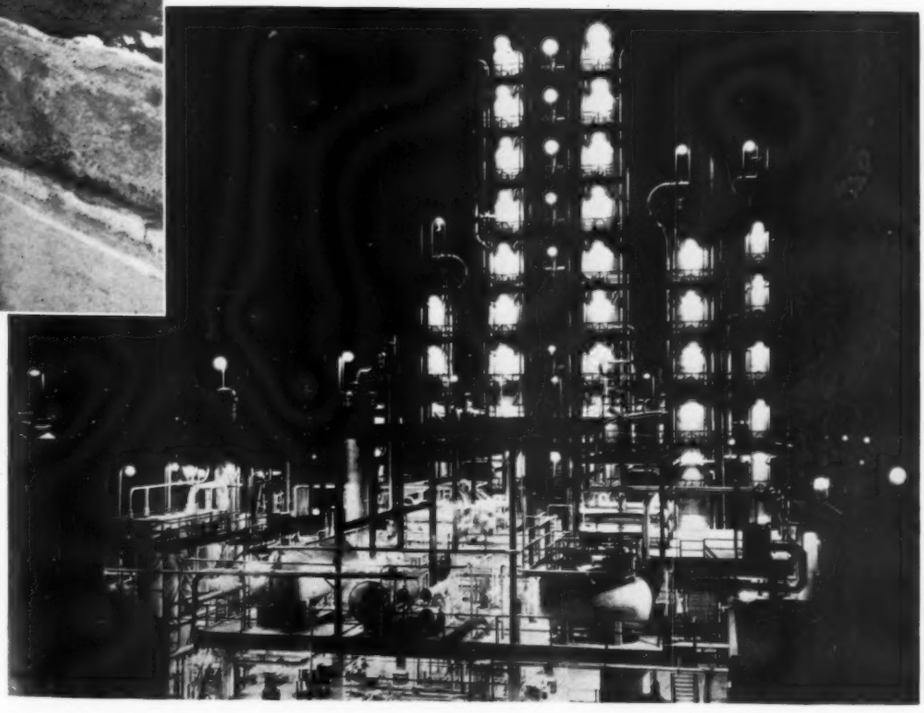
Research to Meet Motorists' Demand for 100-OCTANE FUEL

Trend in Development of Automotive Engines Indicates that Industry Will Soon Be Called Upon to Develop Cheap Motor Fuel of 90 to 100 Octane.

USE of the octane scale for rating anti-knock qualities of automotive and aviation gasolines has now been adopted all over the world. As generally understood, the octane number of a fuel is measured by comparing its performance with that of mixtures of isoctane and normal heptane. The use of mixtures of isoctane and normal heptane as a scale on which to measure anti-knock value was originated in the Ethyl Gasoline Company's laboratories about 1927. Prior to that time anti-knock value of all gasoline was measured by preparing mixtures of a selected straight run gasoline and benzene, and finding what proportion of benzene and the standard gasoline gave the same knock as the gasoline under test; if it knocked the same as a 40-60 mixture of the standard, the gasoline was said to have a benzene equivalent of 60. The present system of isoctane rating did not come into standard use until 1931, when committee D-2 of the ASTM recommended a standard engine known as the C.F.R. engine, together with a standard method of testing.

From about 1938 reports have been published on the average octane numbers of commercial motor fuels, and with few exceptions every year has witnessed an increase in the anti-knock quality of the average American gasoline. This may be seen from the accompanying table, wherein the numbers reported from the earlier years have been recalculated from the old benzene equivalents and reduced to the octane scale now in use.





GASOLINE OCTANE NUMBERS 1928-41

Year	Octane Number
1928	56
1929	60
1930	60
1931	61
1933	65
1934	69
1935	69
1936	69
1937	70
1938	72
1939	73
1940	73
1941	74

Beginning with the winter of 1936 the Cooperative Fuel Research Committee and the U. S. Bureau of Mines have collaborated in a nationwide study of the properties of American commercial motor fuels. In this study the data are obtained from the analysis of samples taken from filling stations all over the country. The samples are collected twice a year in order to represent the winter and the summer grades. During each sampling period about 2,000 samples are collected, representing the products—premium, regular and third grade—of more than 100 large and small suppliers. The analytical report on each sample shows sulphur content, Reid vapor pressure, gravity, octane number (A.S.T.M.), and the distillation characteristics. Numerous laboratories have contributed their services in making analyses, which are sent to the Bureau of Mines for editing and publication. This series of reports has been edited by E. C. Lane from the beginning comprising an interesting record.

With the issuance of the 1941 winter report (Bureau of Mines R. I. 3576) Mr. Lane took occasion to make a five year comparison of the anti-knock and volatility characteristics of the three grades of gasoline sold in the period 1935-36 to 1940-41. The results of this comparison are shown graphically in the accompanying chart. In these curves the premium grade is represented by full lines (P), the regular grade by broken lines (R), and the third grade by dotted lines (T). As may be seen from the graphs, since 1935 the average octane number of the winter regular price gasoline (R) has risen 4.8 ASTM octane units (from 69.6 to 74.4). This rise has been more pronounced during the past two winters than for the three preceding winters. The average octane rating of the winter premium price grade has risen 3.5 ASTM units (from 76.7 to 80.2). A slight decline in the average octane rating of this grade occurred in the winter of 1939-40, but otherwise the rise in the average has been steady. After a slight decline between 1935-36 and 1936-37 the average octane number of third grade gasoline rose steadily from a low of 57.5 to 65.6 in the 1940-41 winter survey. This was a jump of 8.1 points in the ASTM octane number of this grade during the past four years. The present third grade gasoline is now only four octane numbers below the regular grade of 1935-36.

With the rise of octane numbers of these winter gasolines there has been a change in their distillation characteristics. Except for a noticeable increase of the temperature for the 90 percent recovered and 50 percent recovered points of the premium price grade in 1935-37 there has been a fairly consistent drop in the distillation temperatures. This obviously means that gasolines are containing more of the lower boiling fractions. During the five-year period the vapor pressure of the winter regular grade has not varied more than 0.3 lb. either way from the average of about 10.3; on the other hand the vapor pressure of the premium grade has risen 1.1 lbs. (from 9.0 to 10.1); the vapor pressure of the third grade has risen 1.1 bls., from 7.9 to 9.0. Examination of the figures representing the octane history of the premium grade summer

gasolines, in comparison with the winter fuel during the five-year period, shows that in every year the anti-knock rating of this grade has been 0.5 ASTM higher than that of the winter premium grade, except in 1939, when it was only about 0.2 unit higher on the average. The summer gasolines of the regular and third grades also tend to be somewhat higher in octane rating than the corresponding winter fuels. It is curious to note that the vapor pressure of both summer and winter regular grade is higher than that of the premium grade in all years.

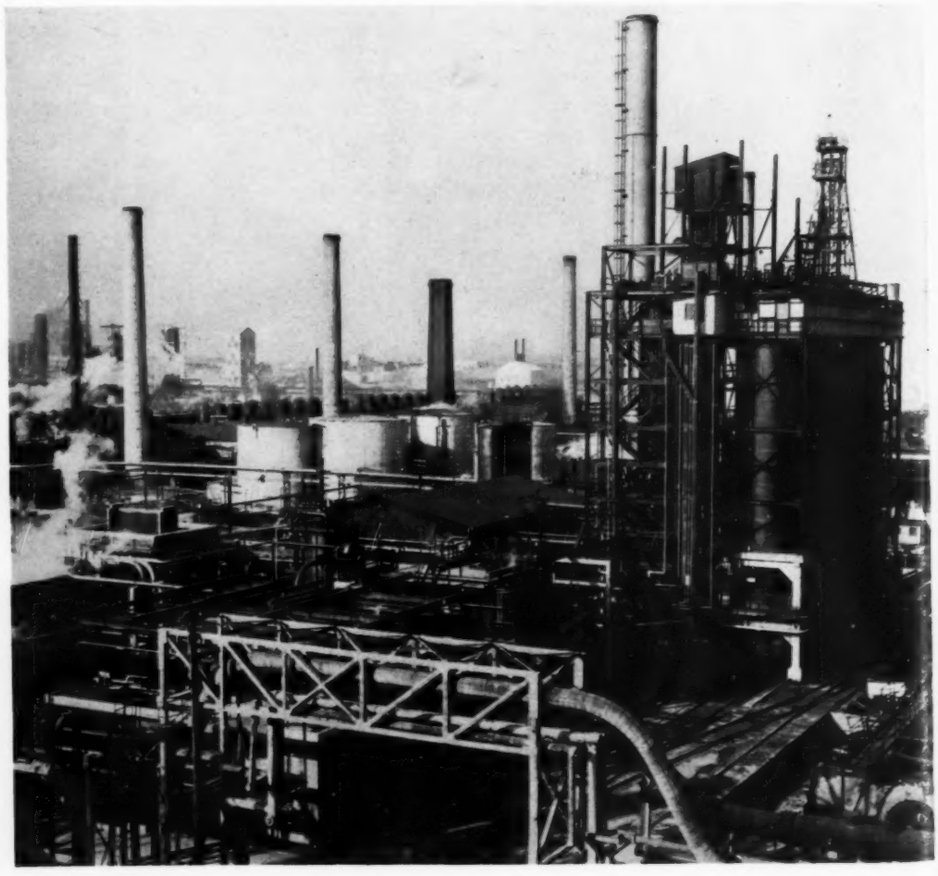
The record thus shows that the average octane number of American commercial motor fuels has steadily increased since at least as far back as 1928. Perhaps the main reason for this growth into the higher octane regions has been competition among refiners to supply the motorists with better gasoline than their rivals are furnishing. The fact is that a gasoline which knocks too much is practically unsalable for ordinary automobile service, and hence every refiner has had to keep his product up to current octane ratings. The necessity which has forced refiners to join in the octane race has been and still is responsible for a rather fundamental change in refining technology. There was a time only a few years ago when the octane rating of ordinary cracked or straight run gasoline could be boosted by adding a little more tetraethyl lead, but as more and more refiners improved their processes and made greater use of high quality blending materials, it became no longer possible to pep up a low grade motor fuel by any amount of tetraethyl lead that could be regarded as economical. For this reason refiners throughout the industry have been forced to install equipment for catalytic cracking, polymerizing, isomerization, alkylation, hydroforming, polyforming, or some other process that would increase the content of isoparaffins and aromatics in their gasolines, which would thus acquire a higher octane number in the clear, and one that can be boosted still higher by economical amounts of tetraethyl lead. This consequence of the octane race has required a great amount of money to be spent on new refinery apparatus merely for the improvement of octane number, without enlarging the total refinery capacity. It is estimated that United States refineries have been spending, on the whole, more than $2,500,000 a month for this purpose alone, besides special equipment that is designed for the production of synthetic rubber, military toluene and other specialties.

Since it is very evident that octane numbers have been and are on the increase, the question arises as to how far they are likely to go; secondary to that is the question as to how refiners may keep up with the demands of the engine builders. How far octane numbers will rise depends in large part on the design of future automotive engines. If the engine builders improve their designs and step up their compression ratios, the refiners will be called on to turn out fuel of higher and higher octane rating. However, there will be in general, no point in furnishing more octanes than the engine requires; for instance, if an automobile runs well on an 80-octane premium fuel the motorist will not gain much by filling his tank with the 100-octane number gasoline required for an airplane engine. But it is quite within the bounds of possibility that in a few years all, or at least the higher-priced automobiles will be designed for 90 or perhaps even 100 octane number fuel; provided, that the refiners can supply this quality at a price that the average motorist will consent to pay for improved performance.

Assuming that octane numbers continue to climb, how is the refiner to stay in the race; or, to what extent is the refining industry now in a position to push octane number of the regular grade above the present 74, and the o.n. of the premium grade over the present 80? There is no technical reason why all automobile gasolines should not at once have much higher average octane numbers. It is merely a matter of equipment and process and market demand. There are quite a number of ways of producing a cracked gasoline with high octane numbers in the clear. To mention one example, Houdry cracked gasoline from reduced crude is turned out with 76-78 o.n. in the clear, which can be economically stepped up to 92 with tetraethyl lead. To mention another, hydroformed gasoline from heavy naphtha comes out from the reforming process with an ASTM rating of 80 octane number, which is subject to increase by addition of tetraethyl lead. But under present specifications for automobile fuel a 92 octane number distillate will not be put on the market directly; it is better used to blend with low grade stuff to produce the present regular and premium grades. When and as the market calls for more and more octanes, the refiner may do one of two things; he will use a larger proportion of his high grade products to work off a smaller proportion of low octane stuff, or he will have to give his low grade products special treatments so that they will need less of the blending material.

Considering the present resources of the refining art there is nothing in sight to prevent the average octane rating of automobile gasoline from continuing its yearly climb until it reaches about 90; it is mostly a matter of using easily available materials for keeping step with the engine designers. For carrying the average octane number of filling-station gasoline much beyond 90 it appears to be necessary to invent new cracking processes suitable for mass production at a low or at least a reasonable cost, and without the necessity of using special blending agents other than tetraethyl lead. Even this reservation is subject to modification if and when it becomes

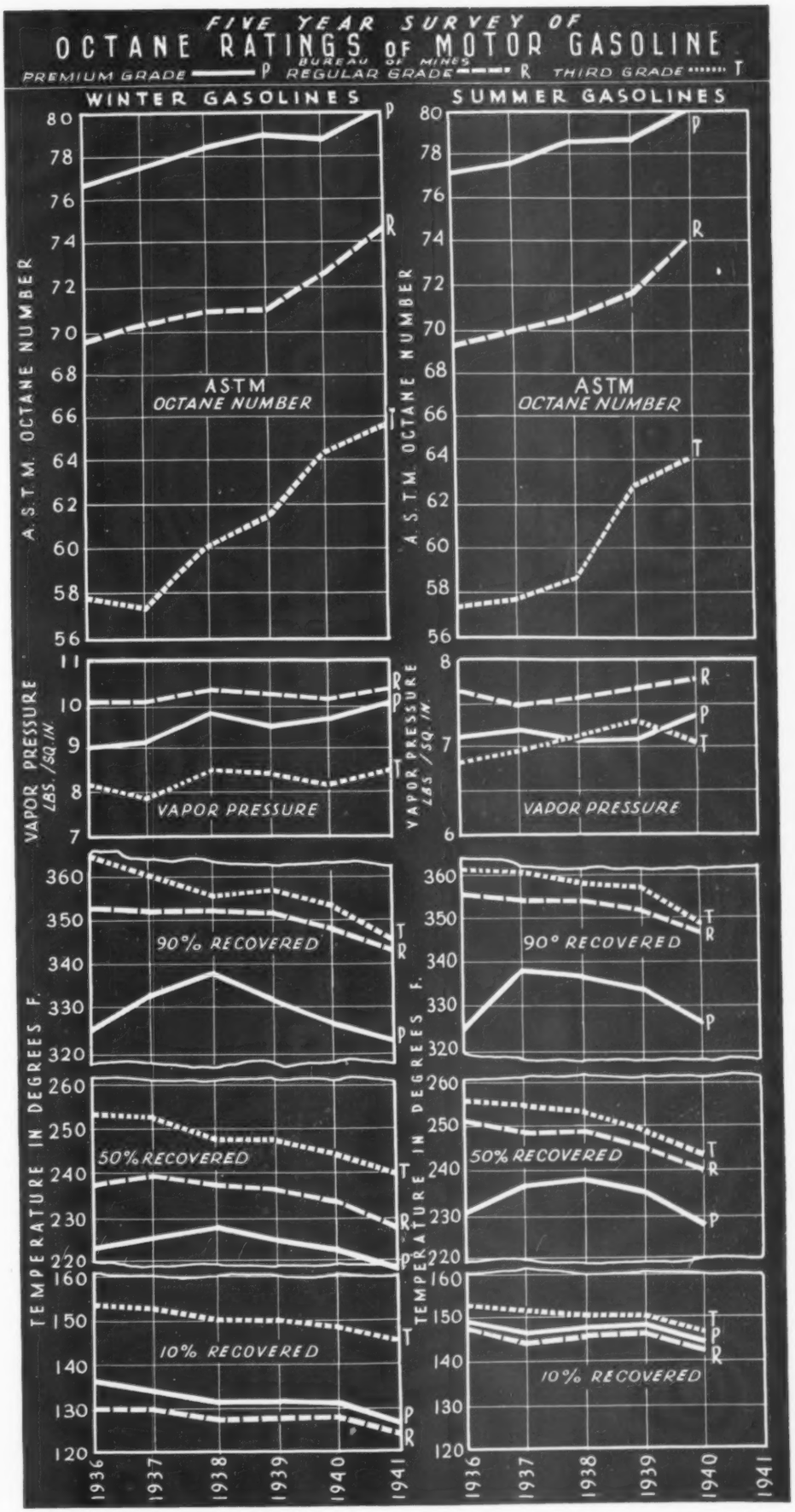
Whiting, Indiana an important center of refinery activities in the middle west: The photograph shows a reduced crude coking unit engineered by the Lummus Company for Standard of Indiana.



possible to make iso-octane, neo-hexane and other high class and high-cost blending agents cheaply enough. In this respect much may be hoped for from catalytic polymer gasolines, some of which have blending octane numbers up to 125, and which might be used to convert a 45 o.n. straight run gasoline to 100 o.n. fuel. Among other prospects that loom ahead is a product which has been named triptane, and which is said to have an o.n. of 150; what its blending value is has not been made clear.

Some interest has been aroused in the question of what is to be done with the greatly increased facilities that are being prepared for the production of 100 octane number aviation gasoline required for the military needs of the United States and associated nations in the conflict with the Axis. How much of this product will be called for will depend on contingencies. Military experts have estimated that for a full-scale war effort the United States will need 9,000,000 bbl. of 100 o.n. gasoline annually. This is relatively a small quantity, hardly above one percent of all motor fuels consumed in the United States in 1940. Much of the new production of 100 o.n. fuel, will be taken off the producers' hands by the government at prices that will amortize the equipment in five years. With the installations paid for, the refiners might use this high grade material in blending to produce the quality of fuel required for the improved automobile engines of the post-war period, and perhaps for a possible great expansion of aviation transport.

At the present moment 23 out of the 460 refineries of the United States are producing 100 o.n. aviation gasoline; 10 others are making aviation fuel of 87 to 92 o.n.; some of the navy planes use this grade. The current production of 100 o.n. fuel by all refineries is about 40,000 bbl. a day. It is expected that this will soon be raised to 54,000 bbl. when new refining facilities now building or planned come into production. The present capacity is already more than sufficient for meeting the current demand; the new capacity is being provided in view of possible future needs. Lately the military authorities have revised their wants drastically upward, especially in view of expected British and Russian requirements. The only difficulty that could stand in the way of an annual production of 20,000,000 bbl. a year, or more, is lack of equipment of which the design and operation is already known. The industry requires only time necessary for installing the necessary facilities and an assurance that its investment will be amortized. The most recent pronouncement of the petroleum coordinator contemplates the erection of 50 new plants for the production of 100 octane number gasoline and an unspecified number of byproduct plants, the whole estimated to cost $150,000,000.



Charts based on data collected by the Cooperative Fuel Research Committee and the U. S. Bureau of Mines showing properties of representative commercial motor fuels distributed in the United States.

Refiners To Concentrate On 100-OCTANE

By J. C. Morrell & Gustav Egloff

Universal Oil Products Company
Chicago, Ill.

Processes that Assure U. S. of Continued Leadership in Production of 100-Octane for Aviation Fuel Reviewed—Capacity May Be Trebled to Meet Huge War Demand

IT IS doubtful whether any single commodity is as important in determining the outcome of the present war as 100 octane aviation gasoline. In view of the critical importance of high octane aviation fuel in the affairs of the world today a review of the technical methods and processes for the production of this valuable product is considered timely and is here undertaken.

The United States has led the world not only in the production of high octane aviation gasoline, but also in the development of processes for producing it. It is estimated that the volume of 100 octane gasoline produced in the United States at present is in excess of 40,000 bbl. per day, and facilities for producing an additional 6,000 bbl. per day are in the course of construction. The coordinator of the United States oil industry predicted a shortage of 100 octane gasoline unless the producing capacity were trebled so that the present objective is 120,000 bbl. per day of 100 octane gasoline.

The various technical processes for the production of high octane gasoline depend in general on the improvement of stocks, e. g., straight-run gasoline produced from highly selected crude oils to produce a blending stock; fractions of straight-run gasoline or cracked naphtha by hydroforming; catalytic cracking and hydrogenation; or by production of isooctanes and products such as alkylates from gases, either cracked or natural. Blending stocks such as isopentane and neohexane are used to improve volatility and tetraethyl lead is added to improve the octane number. Aviation gasoline of approximately 87 octane may be made up of varying percentages of these components and the blend may be raised to 100 octane by adding 3 cc. of tetraethyl lead. Straight-run gasoline suitable for blending stock may be derived from highly selected crude oils such as those from the Gulf Coast and California. Octane ratings of debutanized 300 deg. F. endpoint straight-run gasoline range from 70 to 76. Isopentane is obtained by close fractionation of natural gasoline and has an octane rating of 90. Isooctane aviation gasoline stock of 95 octane may be obtained by the polymerization of iso and normal butylenes to form isooctenes, which are then hydrogenated to isooctanes. Gasoline stock is obtained by the alkylation process having from 91 to 95 octane, as a result of the chemical combination of isobutane and butylenes by the use of sulphuric acid as a catalyst. Neohexane of 94 octane rating is made from the thermal alkylation of isobutane by ethylene under relatively high pressure. Isobutane may be obtained from natural gas, fractional distillation of natural gasoline, cracking of oil and naphtha, and more particularly from isomerization of normal butane. Olefins such as butylenes are produced by cracking and by catalytic dehydrogenation of butanes. The alkylation process is at present the principal one for manufacture of blending materials for 100 octane aviation gasoline. The key hydrocarbon for alkylation is isobutane and the requirements for this must be made up in part by isomerizing normal butane. The principal technical processes for the production of aviation gasoline are described in the following article.

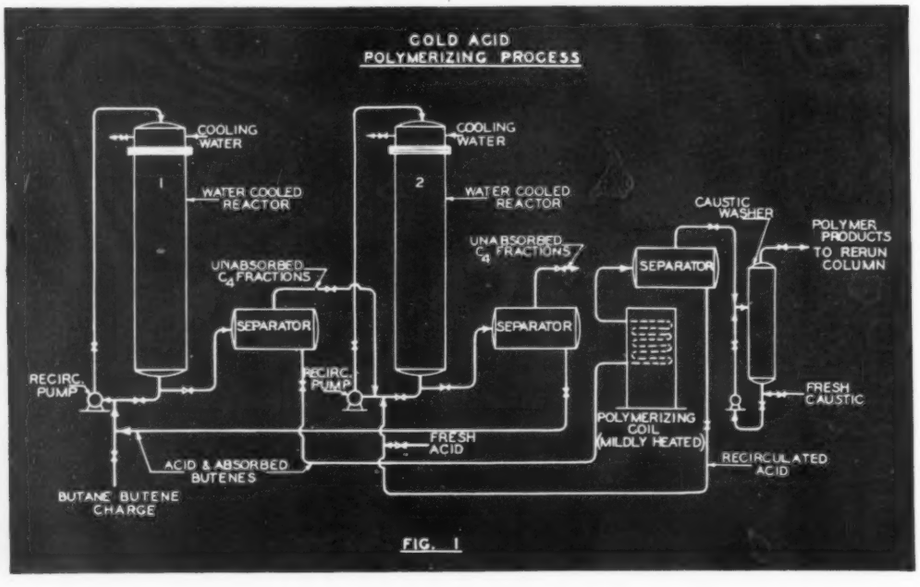


FIG. 1

In the production of isooctene from isobutylene on a commercial scale the original process employed cold sulphuric acid, which was later supplanted by the hot acid process. The cold sulphuric acid polymerization process is shown in Fig. 1 and consists of an absorption section and a polymerization section. Isobutylene in liquefied state is contacted with sulphuric acid with 60 to 70 percent concentration at temperatures of 65 to 80 deg. F. in two stages and by countercurrent flow. The absorption is an equilibrium reaction which depends upon the amount of isobutylene absorbed, the acid strength, and temperature. Under proper operating conditions as much as 90 percent of the isobutylene may be absorbed without any appreciable absorption of normal butylenes. In view of the fact that the hot acid process produces a much larger yield of isooctenes from which octanes may be produced, it has supplanted the cold acid process.

The Shell and Standard Oil Development Companies have a process for producing isooctene from the butenes present in cracked gases wherein sulphuric acid is employed as a catalyst at elevated temperatures. In this process both normal butene and isobutene react to form isooctene. An excess of normal butene is usually present. The process is shown in Fig. 2. In carrying out the operation of the process, the charge of butane-butene fraction and the acid reagent are introduced into the recycling line of the hydrocarbons undergoing treatments. Fresh acid is also added. The mixture of recycle stock, fresh acid and butane-butene fraction is discharged into a cooler and then to a time reactor, in which the polymer is produced. The reaction is exothermic, and sufficient cooling is provided to maintain a temperature of about 175 deg. F. In present practice acid concentration is about 70 percent for a 10 to 15 minute time of contact. The mixture of hydrocarbons, polymer and acid, leaves the time reactor and flows into a separator where most of the acid is removed by gravity. The hydrocarbon and polymer stream leaving the separator is further cooled and passed into a final acid separator. The polymer is then debutanized. The polymer product is mixed with caustic and heated with exhaust steam to neutralize acidic substances and to hydrolyze acid sulphates. After

the removal of caustic soda, the product is passed to a second debutanizer, after which the dimers are separated from the heavier polymers and delivered to storage. The polymer product formed is stated to be about 90 to 95 percent octanes, which upon hydrogenation have an octane value of about 95. The yield of octenes is said to be equal to twice the isobutene content of the feed stock when there is more normal butene than isobutene present in the original stock, which is usually the case.

Polymerization of olefinic hydrocarbons is one of the most important industrial catalytic reactions. In one of its aspects it is used to produce motor fuels and is referred to as non-selective polymerization when mixtures of olefins are employed; for example those contained in cracked gases. When normal and isobutenes are employed as charging stock the process is referred to as selective polymerization. The Ipatieff catalytic process employing solid phosphoric acid catalyst is widely used for the production of high octane polymer gasoline and isooctane, the latter being the product of selective polymerization followed by hydrogenation. Selective polymerization employs temperatures of approximately 300 deg. F. and 700 lbs. per sq. in. pressure, the temperature being somewhat lower and the pressure higher than in non-selective polymerization. The isooctenes have an octane rating of 84 and on blending, a value in excess of 150. The isooctanes produced by hydrogenation have octane ratings of from 95 to 98 and individual octanes have values in excess of 100. Isooctane gasoline is of extreme importance in aviation, both for commercial and military planes. The isooctanes are blended with lower-boiling petroleum fractions for starting, and a small amount of ethyl fluid to raise the octane value to 100. An improvement in power output of 30 percent is shown with 100 octane fuel compared with 87 octane. The saving in pay load for large commercial air transports may be several thousand dollars. Millions of barrels of isooctane are produced currently per year with ever increasing amounts for the needs of military aviation. In the operation of the process the charge is heated to the required temperature, then passed through the tubes filled with the solid phosphoric acid catalyst, where the polymerization reaction occurs. The polymer product leaving the last catalyst vessel is cooled and charged directly into the stabilizer. The isooctenes are hydrogenated to produce isooctanes. However where it is desired to use butanes as raw materials they must be dehydrogenated first, then polymerized and hydrogenated in accordance with the process described in the following paragraph and illustrated on the following page.

The dehydrogenation-polymerization-hydrogenation process for the production of isooctane is illustrated by flow diagram, Fig. 3. This process is also applicable to the production of aviation fuel from mixtures of iso and normal butanes. Fig. 4 is a flow diagram of the dehydrogenation

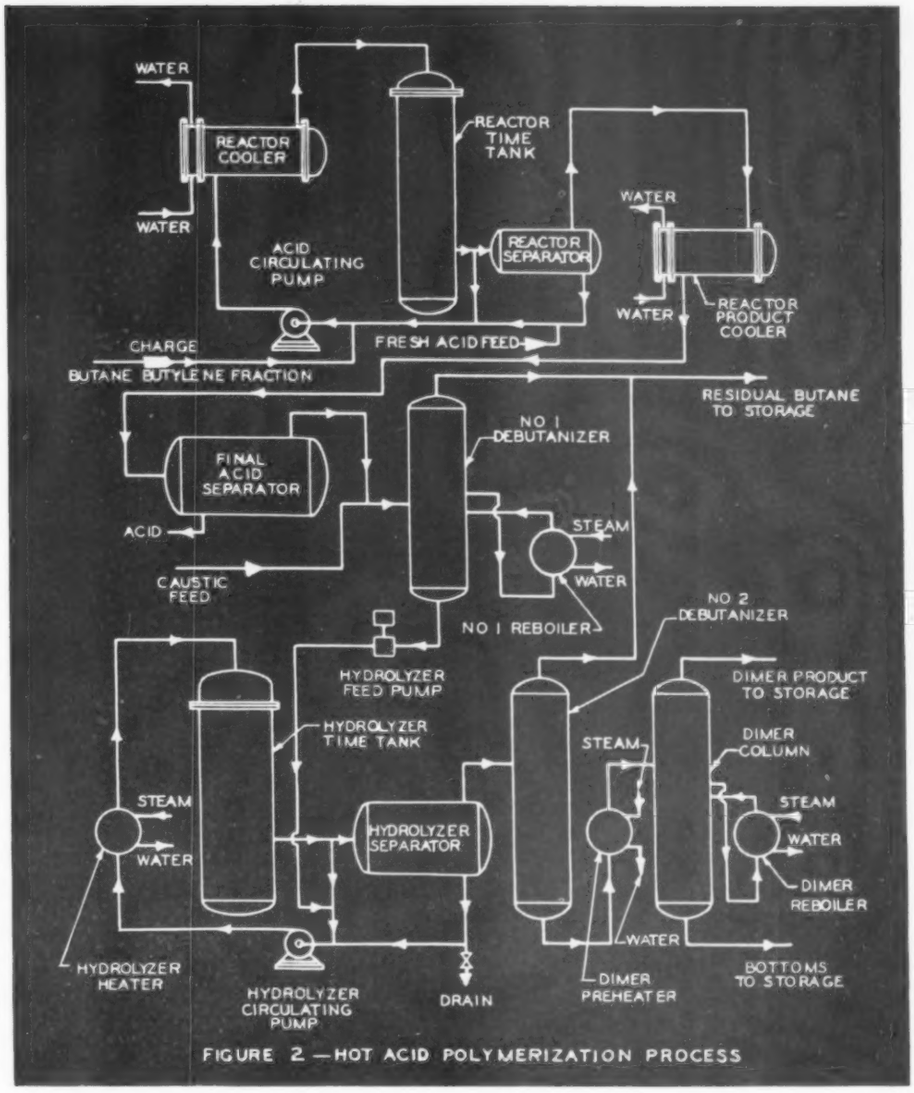


FIGURE 2—HOT ACID POLYMERIZATION PROCESS

step and Figs. 5 and 6, respectively, represent one stage of catalytic polymerization and the hydrogenation step. Charging stock consists essentially of butanes. The proportion of isobutane to n-butane varies from 15 to more than 75 percent. Octane rating of the hydrogenated polymer increases with the increase of isobutane in the charge. Butanes are supplied at relatively low pressure to the preheater of the dehydrogenation unit, from which it emerges at approximately 1075 deg. F. and is directed to the dehydrogenation catalyst zone. The catalyst is of chromium oxide on alumina and is contained in vertical tubes externally heated by hot combustion gases. The butane passes through the catalyst at a high space velocity, and approximately 25 percent of the charge is dehydrogenated. Gases leave the catalyst tubes at a pressure only slightly above atmospheric and at a temperature of approximately 1130 deg. F. The butane-butene mixture and hydrogen from the dehydrogenation system are cooled and compressed to approximately 100 to 200 lbs. per sq. in. and then are passed to an absorber, where the hydrogen is separated. A stripper is provided for removing the butane-butene mixture from the absorption oil, which is cooled and returned to the absorber.

The butane-butene product is pumped at high pressure to the polymerization unit of the process employing the solid U.O.P. phosphoric acid catalyst. The temperature employed here is 250-350 deg. F. and the pressure 750 to 1,500 lbs. per sq. in. Temperature is controlled by vaporizing water under pressure in a jacket or shell around the reactor tubes. At higher temperatures a greater proportion of the normal butenes is polymerized, but a hydrogenated product of lower octane number is produced. The temperature, therefore, is determined by the octane number of the product desired. Steam produced in the reactor jackets, because of the exothermicity of the reaction, is used to preheat the feed. The polymer is debutanized, distilled, and catalytically hydrogenated to end-point aviation gasoline at approximately 97 octane number. Only about 10 percent bottoms (heavy polymers such as trimers) are recovered as a residue. The unreacted normal butenes from the debut-

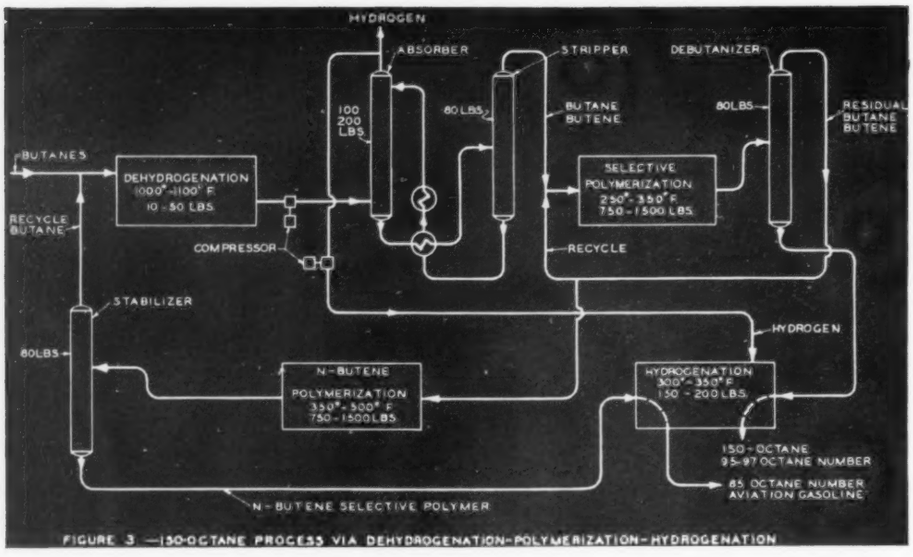


FIGURE 3.—150-OCTANE PROCESS VIA DEHYDROGENATION-POLYMERIZATION-HYDROGENATION

anizer are led to a secondary polymerization stage, generally operated at higher temperature (i. e. 480 deg. F.) than in the selective polymerization section. Temperature control is similar to that in the selective polymerization operation. The polymer product of the normal butene polymerizing step passes through the stabilizer where liquid polymers are separated from butanes. Butanes are returned to the dehydrogenating step of the process. The polymer formed in the normal-butene polymerizing step when rerun and hydrogenated yields a product of approximately 85 octane number. The hydrogenation unit is operated alternately on the selective polymer and the residual butene polymer. A nickel catalyst is employed for hydrogenation. The hydrogen reproduced by dehydrogenation of the butanes is twice that required for hydrogenation of the polymer products. The rerun polymer and the hydrogen gas are supplied at a pressure of 150 to 200 lbs. per sq. in. to the hydrogenation reactor tubes. As the nickel catalyst is sensitive to sulphur compounds, it is preferable to desulfurize the butane before dehydrogenation. If the butane is not desulfurized, polymer supplied to the dehydrogenating step is first passed through a guard reactor, which is filled with spent hydrogenation catalyst for removing sulphur compound impurities, and then is passed through two reactors in series, being hydrogenated by the gas in countercurrent flow. As hydrogenation is also an exothermic reaction, essentially the same method of temperature control is used as in the phosphoric acid polymerization process. The temperature is maintained at approximately 350 deg. F., and the outlet pressure sufficient to depress the vaporization of excessive amounts of isooctane in the spent gas. The hydrogenated product from the selective polymerization step consists essentially of isooctanes with minor quantities of other products.

The isooctenes produced may be converted into isooctanes by the U.O.P. low-pressure hydrogenation process at inlet pressures of from 75 lbs. upward and temperatures of 320-350 deg. F. in the presence of a nickel catalyst. The hydrogenation reaction is also exothermic; hence the unit is similar in design to the selective polymerization unit in respect to close temperature control by means of a water jacket around the reactor. A flow chart of the low-pressure hydrogenation unit is shown in Fig. 6. The isooctanes as produced are not aviation gasoline as such. They must be blended with aviation stock, such as special straight-run or natural gasoline, and isopentane for volatility. The usual procedure for preparing 100 octane aircraft fuel is to blend commercial isooctane with aviation straight-run gasoline and isopentane, and add 3 cc. of tetraethyl lead per gallon. The isopentane is used to supply the front-end volatility which isooctane lacks. The amount of isopentane incorporated in the finished blend is usually 10-15 percent, depending upon its availability and also on the vapor pressures of the base fuel.

One of the important commercial methods for the production of high-octane aviation fuel is the alkylation process employing sulphuric acid as a catalyst. This process has been discussed in a paper by Anglo-Iranian, Humble and Shell at the 1939 annual meeting of the A.P.I.; also in Monnell's U. S. Patent No. 2,169,809 of August 15, 1939. The reaction involved in this process is the direct addition of an olefin, for example, butene, to isobutane to form isoparaffins. This is readily accomplished by contacting the olefin with a large excess of isoparaffin in the presence of a relatively large amount of sulphuric acid at an approximate temperature range between 30 and 85 deg. F. employing sulphuric acid concentrations of approximately 90 to 100 percent. Aviation fuels with octane ratings of 92-94, and in some cases higher, may be made by the use of this process; and, with the development of isomerizing processes to augment the volume of isobutane available by the treatment of normal butane, the potential yields of isooctanes by alkylation from the average refinery is greater than by the alternative method of making isooctanes, namely, by the two-stage process of olefin polymerization followed by hydrogenation. The alkylation process fits in well with many refinery operations, and the materials of construction and type of operation required are simple and in line with ordinary refinery operations. To prevent the absorption step from proceeding to the point where the acid becomes useless, it has been found necessary to have a large excess of the isoparaffins.

In continuous operation the suppression of olefin absorption is brought about first by diluting the olefin feed with isoparaffins and then adding this mixture to an emulsion of acid and reacted hydrocarbon which is rich in isoparaffins and substantially olefin-free. In commercial plants mixing is performed by the use of a circulating pump and intimate contact is main-

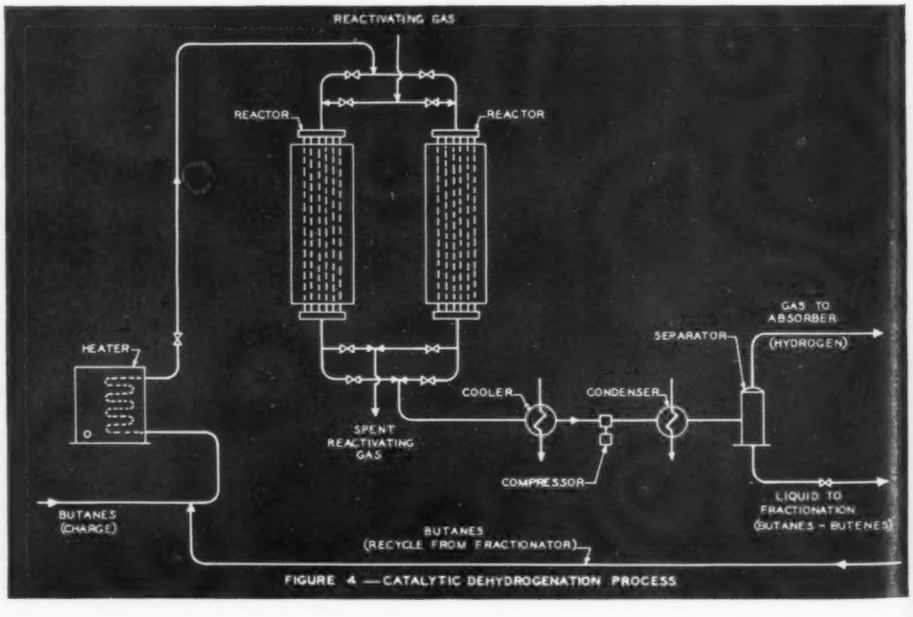


FIGURE 4.—CATALYTIC DEHYDROGENATION PROCESS

tained by the velocity of flow through baffles or jets. A simplified flow diagram of a commercial plant is shown in Fig. 7. The acid is withdrawn at approximately 90 percent concentration since there is a drop in acidity from approximately 98 to 90 percent or lower, due to absorption of hydrocarbons in the reaction, although other reactions may be contributing factors. The spent acid withdrawn is replaced by fresh acid, thus maintaining the efficiency of the operation. The quantity added is affected both by the composition of the feed stocks and by operating conditions. From one viewpoint, acid is not consumed but is diluted by the hydrocarbon, and a major part of the acid can be recovered by ordinary reconcentration methods, or it may be used for acid-treating various products of the refinery. Isobutane is the isoparaffin used in the process, since isopentane and isohexane are in themselves valuable components of gasoline. The charging stocks to be converted are preferably treated with a caustic wash to remove hydrogen sulfide and possibly other impurities. Amines may be removed by water washing. The operating variables are isoparaffin-olefin ratio, contact time, acid strength, temperature, acid-hydrocarbon ratio, olefin concentration of the feed and degree of agitation. These variables are interdependent. The isoparaffin-olefin ratio has a marked influence on the life of the acid and on the yield and quality of the product. The higher the ratio the better the results. Usually a 5:1 initial ratio is chosen as the preferred operation with isobutane and butenes. This ratio is, of course, very much higher in the mixture actually undergoing reaction. These high ratios are obtained by blending olefin and isobutane and by recycling the unreacted isobutane. Although the ratio of isobutane to olefin is high, the actual reaction of isobutane is theoretical. As pointed out previously, the isomerization process for the conversion of normal butane to isobutane will, no doubt, be a determining factor in the widespread

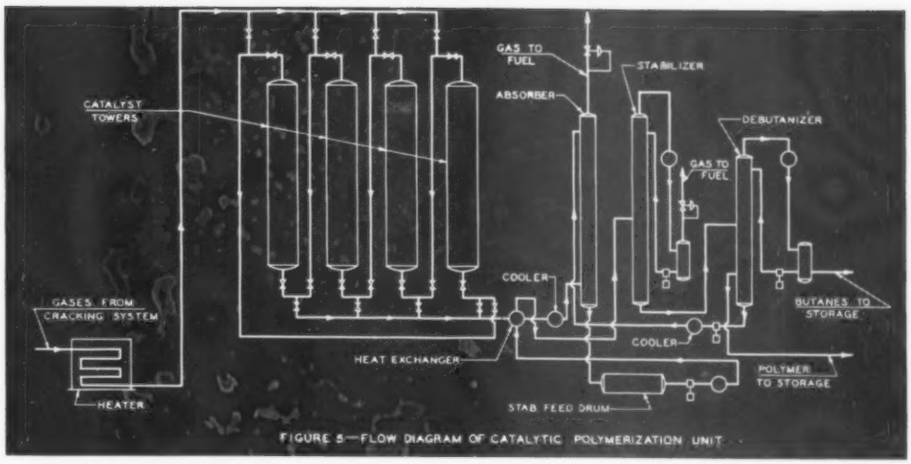


FIGURE 5—FLOW DIAGRAM OF CATALYTIC POLYMERIZATION UNIT.

use of this process. The contact time is usually expressed by the ratio of the volume of hydrocarbons in the reaction zone to the volume of hydrocarbon feed per unit of time. Contact times of 5 to 50 minutes have been considered. The make-up acid strength varies between 96 and 100 percent. There is considerable difference between the actual strength in the reactor and the make-up acid due to accumulation of hydrocarbons and some water, which may be present. The usual acid strength in the reactor has a titratable acid from 80 to 90 percent, but this is different from the acid which is diluted with water to this extent owing to the character of the acid derivatives with which the acid is diluted. Therefore, the true acid strength may be somewhere between 90 and 98 percent.

When temperatures much above 70 deg. F. are employed, increasing oxidation of the hydrocarbons results. Therefore, lower temperatures favor increased catalyst life and better yields of the desired products. Temperatures between 30 and 50 deg. F. have been found satisfactory. The volume of acid to hydrocarbon is usually about 1:1, but ratios as high as 2:1 have been used with good results. Various types of mixing devices have been found satisfactory, e.g., agitation by pump and recycling through a system of jets or baffles gives a simple and good method of carrying out the operation. The products yielded by the alkylation process are highly suitable as aviation fuel because of their high octane number, high lead susceptibility, low sulphur content, and other desirable motor requirements. When isobutane and butenes are used, the product boils almost entirely in the gasoline boiling range with from 80 to 90 percent below 300 deg. F. The product is free from gum and no substantial change occurs on prolonged exposure to sunlight and air.

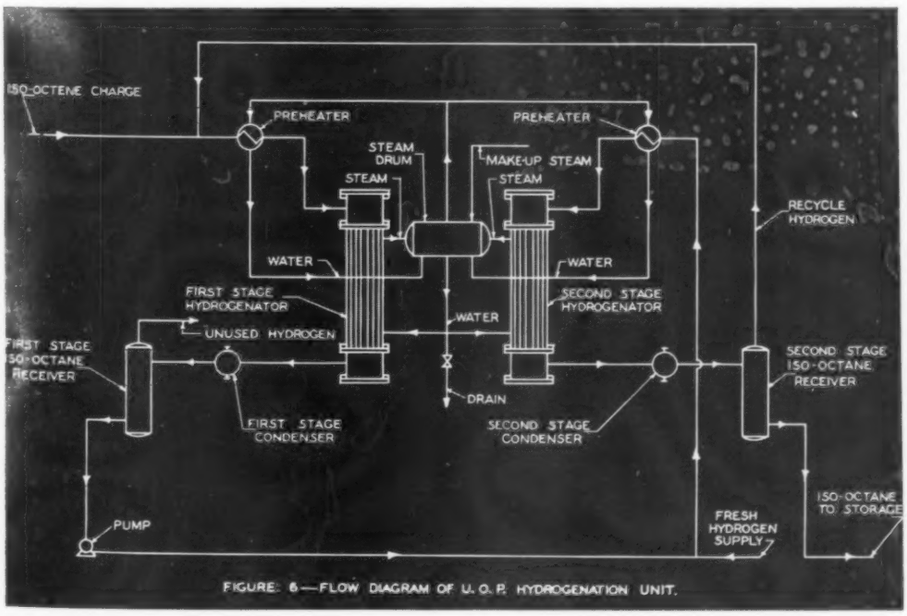


FIGURE 6—FLOW DIAGRAM OF U. O. P. HYDROGENATION UNIT.

The isomerization process has advanced to the stage of commercial operation, particularly under the impetus of the requirements of isobutane for the alkylation process. Fig. 8 is a flow diagram of the process. Normal butane is converted in the presence of a catalyst to isobutane in the following manner. Normal butane in vaporous condition and at a relatively moderate temperature is passed through a granular bed of catalyst, the principal component of which is aluminum chloride. Dry hydrogen chloride gas is introduced with the butane vapors for the purpose of activating the catalyst and in assisting in the reaction. Converted and unconverted butanes and hydrogen chloride vapors discharged from the catalytic zone are condensed. This permits recovery of hydrogen chloride as well as the products of treatment by means of a stripping tower to which the condensed materials are supplied. The stripping column has a reboiler at its base and a refrigerator condenser at the top to provide reflux. The charge containing normal butane is dried before treatment with the catalyst and the flow may be divided into several catalyst chambers and recombined later. Butanes free from hydrogen chloride flow from the base of the column and hydrogen chloride is recovered from the top. The butanes may be recycled to catalyst chambers or sent directly to the receiver.

The purpose of the hydroforming process is to increase the octane number of gasoline from

straight-run as well as cracked naphthas by the use of a catalyst and in general, the type of chemical reaction which occurs is referred to as aromatization. Generally the product gas is recirculated in order to increase the concentration of hydrogen in the reaction zone. The reaction is also accompanied by desulfurization of high sulphur charging stocks. In addition to the production of high octane naphthas suitable for blending to make aviation motor fuels, toluene and other aromatic hydrocarbons may be produced and separated if desired. One commercial plant of 75-100 bbl. per day capacity, operated on 40-45 octane heavy naphtha, produces an 80 percent yield of an 80 octane gasoline. In the operation of the process, illustrated in Fig. 9, the charge is passed through a heat exchange system and then through a heated coil generally above atmospheric pressure. The heated charge is combined with recycled and reheated gas from the gas separator and the heated mixture is introduced into the catalytic reaction zone where conversion takes place to form high octane gasoline, gas and some heavy polymer. A portion of the gas is recycled and the remainder is sent to the absorber. The gasoline and heavy polymer product are charged to a stabilizer, the overhead from which is the high hydrogen gas product. The gasoline may be fractionated into two fractions, the lighter cut comprising an aviation fraction. When deposition of carbon on the catalyst makes it necessary to regenerate the catalyst the material undergoing treatment is switched to another chamber and the catalyst is reactivated in a relatively short time.

One of the most important developments in catalysis as applied to the petroleum industry is the catalytic cracking process to improve the quality of gasoline produced from heavier oils. Yields of 85 percent of gasoline of 81 octane have been obtained from Mid-continent gas oil by the U.O.P. process. This yield and quality is based upon a recycle operation, but the extent of recycling is well within commercial practices

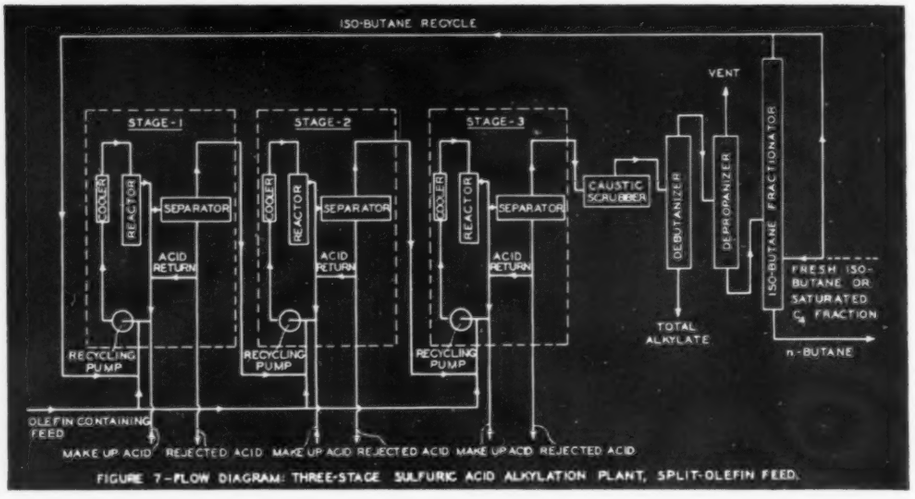


FIGURE 7—FLOW DIAGRAM: THREE-STAGE SULFURIC ACID ALKYLATION PLANT, SPLIT-OLEFIN FEED.

on thermal cracking units. This yield also includes the yield from catalytic polymerizing of cracked gases, 95 percent of which may be polymerized as they leave the catalytic cracking plant. The balance of the charging stock is accounted for by six percent residue oil of 25 gravity and about nine percent unpolymerizable gas and loss. The 85 percent gasoline fraction contains monoolefins and is stable with respect to color and octane value and has about 10 lbs. vapor pressure. As an alternate operation the unit may be run to produce up to five percent isooctenes on a single-pass basis, or 12.5 percent in a recycling operation. The isooctene fraction may be hydrogenated to isooctane gasoline. If the latter is recovered by hydrogenation of isooctenes as an aviation gasoline, the balance of the motor fuel production of about 73 percent by volume will be about 81 octane number.

The plant consists essentially of a heater, catalyst reactor, and automatic controls for alternating the flow of oil through the furnace and reactors, and another section is utilized for reactivating the catalyst. The cycle is about 40 minutes in duration. The results mentioned above were obtained with gas oil, but it should not be understood that operation of the unit is limited to gas oils nor necessarily to overhead stocks. In fact, twenty types of charging oils have been investigated for the purpose of selecting the most practicable catalyst, and the range of stocks tested has extended from Kettleman Hills, California, residuum to Pennsylvania gas oil. Highly paraffinic overhead distillates are favored. By alternating the operating and regeneration cycles, long operating periods may be obtained. The catalyst used is of the alumina-silica type and appears to be exceptionally rugged. Revivification of the catalyst is accomplished by burning off the carbonaceous material which collects on the catalyst, and this in turn necessitates only passing a predetermined amount of air, or mixtures thereof with combustion gases, through the tube and maintaining a moderate temperature of combustion. The oxidation reaction progresses through the reactors under automatically controlled conditions. Prior to burning the carbon from the reactors, they are purged of oil vapors for a period of about 30 seconds. Other types of catalytic cracking processes, such as those involving stationary beds and finely divided catalysts (the flow type of catalytic process) have been developed.

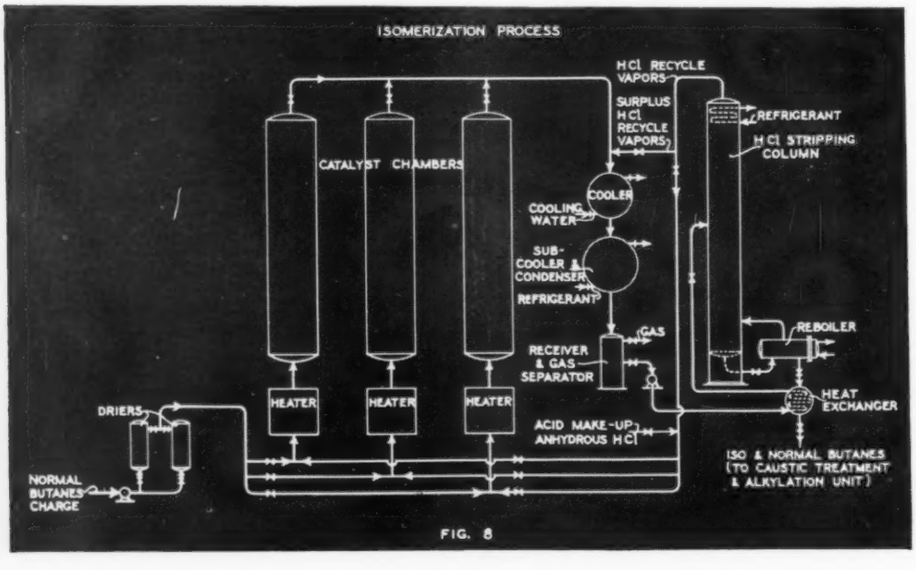


FIG. 8

In the Houdry operation for the catalytic conversion of heavier oils into motor fuels, a 45 percent yield of high-octane gasoline in one pass is obtained. The catalyst employed is stated to be an activated hydrosilicate of alumina. The operation employs two catalyst chambers used alternately for producing gasoline and regeneration, to permit continuous production. The flow diagram, shown in Fig. 10, illustrates the process as operated on crude oil with a single pass through the catalyst, the dotted lines indicating the flow when it is desired to run on a "no residuum operation." The oil is pumped through heat exchangers, where it is preheated with the product from the catalyst chambers, and then to a flash tower where the straight-run products are removed. The residue from the flash tower is

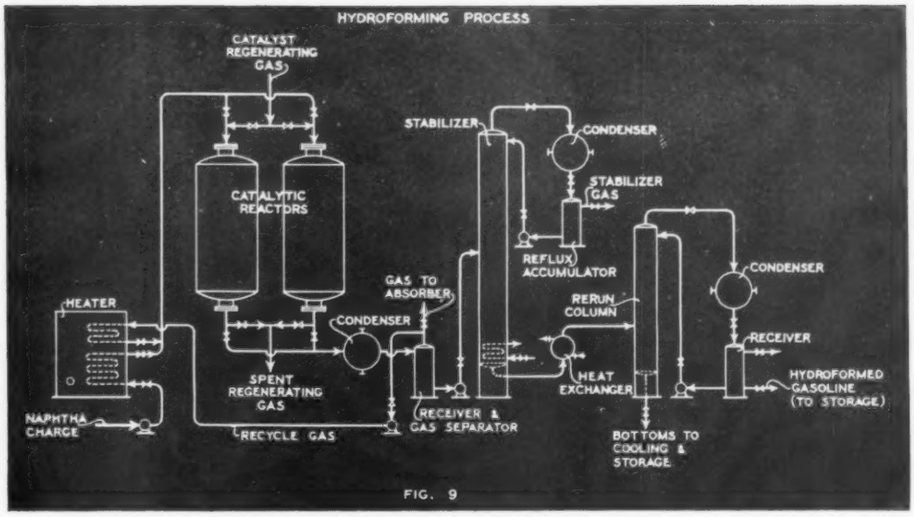


FIG. 9

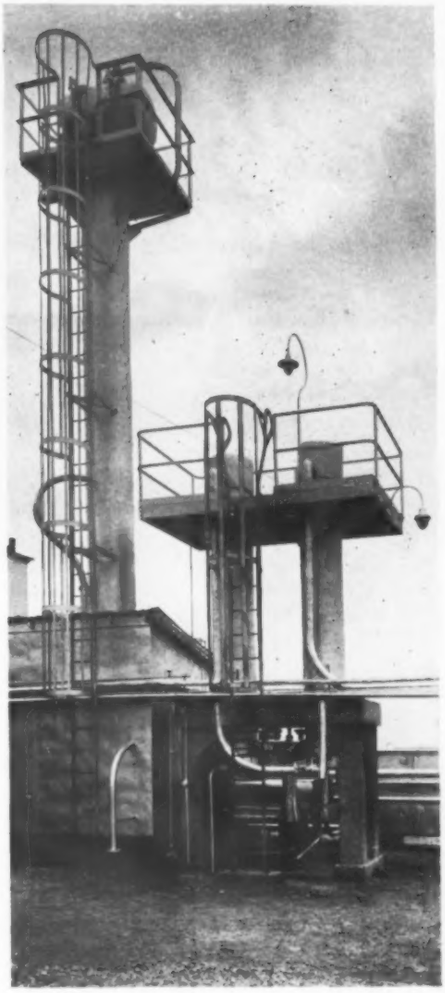
pumped through a heater, where it is raised to approximately 880 deg. F., and from there into a vaporizer. The bottoms are removed as a liquid and the vaporized fraction of the charge is passed to the catalyst chambers. The vapors from the catalyst chambers are heat-exchanged with the crude oil and then passed into the final fractionating tower in which gasoline, furnace oil, and heavy gas oil are separated and withdrawn. The heavier oils may be recycled to the system. When distillates are used as charge, the flash tower and vaporizer may be eliminated. The yield of gasoline from this operation is about 45 percent per pass, based on the charge to the catalyst, having an octane number of from 77 to 81, with blending values of from four to 10 points higher than the actual octane number. The catalyst has a long life and may be readily regenerated. A number of commercial units have been installed.

As shown previously, isooctanes as produced are not aviation gasoline as such. Ordinary commercial isooctane is blended with aviation straight-run gasoline and isopentane, to which blend is added tetraethyl lead. The isopentane supplies volatility. Laboratory inspection data for various blends show that a commercial 100 octane (Army method) seven pound vapor pressure blend could consist of 40 percent of 95 octane isooctane, 45 per cent of 74 octane aviation straight-run, and 15 percent of 90 octane isopentane. To produce a similar blend to equal 100 octane by the motor method, part of the straight-run would have to be replaced with isooctane, for example, 45 percent of isooctane, 40 percent of straight-run, and 15 percent of isopentane. The following interesting comparison of critical properties of 100 octane vs. 87 octane gasoline in airplane performance, using a reconnaissance bomber, is taken from the Institution of automotive Engineers, Australia, The Modern Engineer, July 20, 1941.

The amount of aviation gasoline thus available based on the raw materials needed, even allowing for their diversion for many other uses when employing one or more of the above processes, for example isomerization of normal butane and alkylation of the resulting isobutane with butenes to produce alkylate, will be ample for present or future needs of 100 octane aviation fuel during the wartime emergency.

Aircraft	87 Octane	100 Octane
Max. speed at 2,750 rpm	236 mph	260 mph
Altitude for max. speed	15,700 ft.	17,300 ft.
Rate of climb at sea level	1,490 ft./min.	2,180 ft./min.
" " " " 6,500 ft.	1,630 " "	2,360 " "
" " " " 19,500 ft.	1,220 " "	2,050 " "
Time of climb to 6,500 ft.	4.2 min.	2.9 min.
" " " " 26,000 ft.	19.4 "	12.2 "
Engine		
Maximum output	830 hp	1,050 hp
Maximum power height	14,450 ft.	15,580 ft.

The military advantage of 100 octane gasoline is obvious.



Non-selective U. O. P. catalytic polymerization unit charging 200,000 cu. ft. of cracked gas per day.

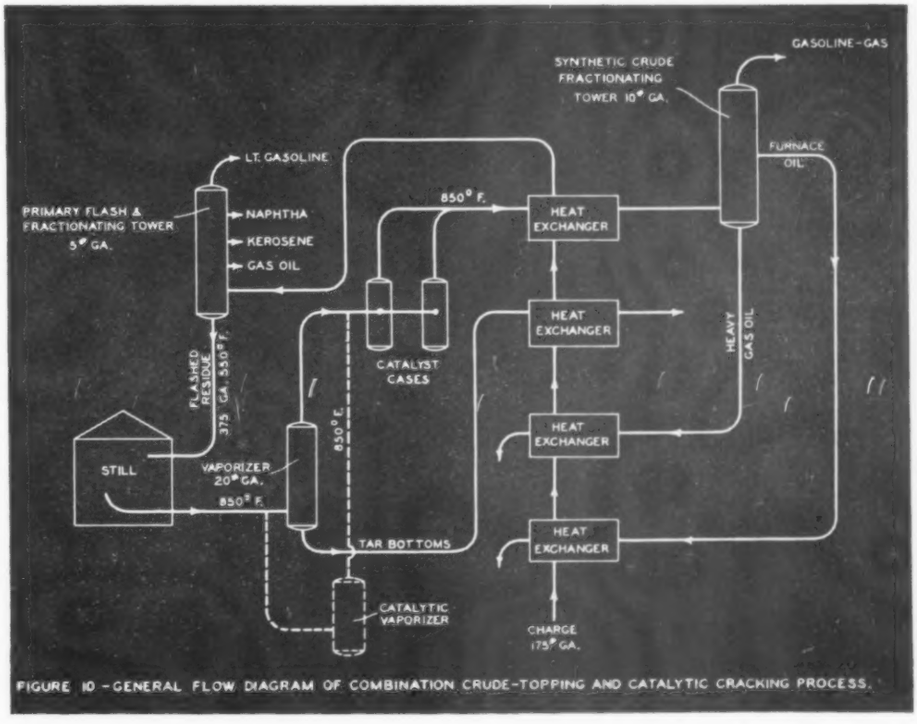


FIGURE 10 - GENERAL FLOW DIAGRAM OF COMBINATION CRUDE-TOPPING AND CATALYTIC CRACKING PROCESS.

TRUE VAPOR PHASE Process in Advanced Stage of

Six Months Operation of North Tonawanda Reforming Unit Confirms Technical Soundness of New T.V.P. Process

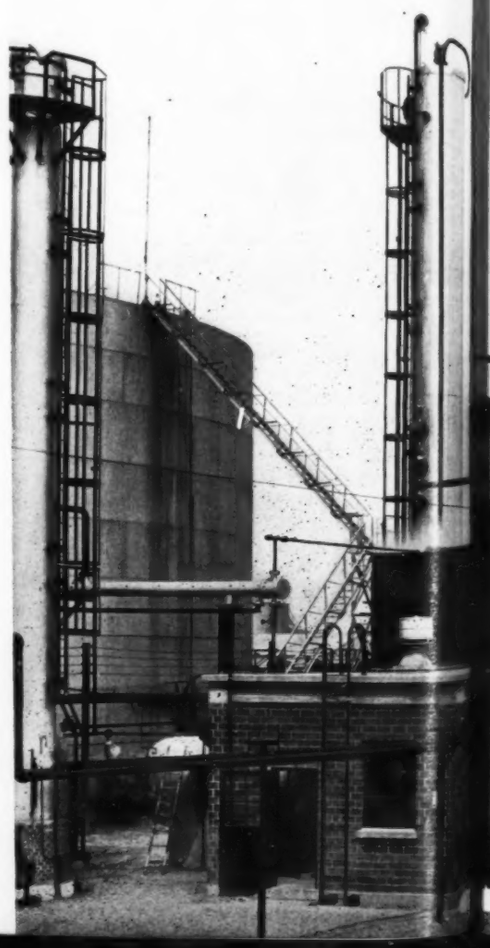
WITHIN the past few years some notable contributions have been made to the art of producing high quality motor fuels by catalytic cracking and other highly specialized processes. This is all to the good, but it will be unfortunate if the progress made in catalysis should spread a feeling that thermal cracking has entered a stage of obsolescence, or that thermal cracking has been found incapable of further improvement. It is still a fact that most of the high octane fuels produced in this country are the product of thermal processes, and it is also a fact that a large number of the 426 petroleum refineries of the United States find it inconvenient to make the large investment required for a catalytic process, which means that not every refiner could use catalysis even if he wanted to, nor would it be desirable to do so.

A recent development which gives point to the statement that thermal cracking is not obsolescent is the first commercial installation of the new true vapor phase process (TVP), which has started a career of evident usefulness in the North Tonawanda refinery of the Frontier Fuel Oil Corporation of Buffalo, N. Y., where it is offering a solution to the problem of obtaining a high octane product at low investment and operating cost. The process is licensed by the Petroleum Conversion Corporation. As installed at the North Tonawanda refinery, the new TVP process may be broadly described as a combination of vapor phase thermal cracking with simultaneous gas pyrolysis. Heretofore, vapor phase cracking, in general, has been regarded as subject to certain disadvantages, among which has been reckoned the formation of large amounts of gas; mainly for that reason it has not in all cases been able to compete successfully with other types of thermal cracking. In the TVP process this disadvantage of excessive gas formation is avoided to a large extent by delivering heat to the vaporized cracking stock by means of a recirculated, highly heated gas stream. After six months of operation there has been accumulated a background of commercial data that confirms the technical soundness of this process and the equipment designed for its commercial application. As this installation represents the TVP in its most advanced stage of commercial employment it will be of interest to give it a brief description in connection with the accompanying simplified flow sheet. Average yield and operating data over a typical 30 day run are given in Table 2 and the utilities in Table 3.

The cold charge, which usually is heavy naphtha, is pumped to the top of an absorbing column operating at 150--200 lbs. gauge, through which it descends counter-currently against rich gases from a reflux accumulator beyond the scrubber-fractionator. The unabsorbed portion of this gas passes out of the system at the top of the absorber as product; the bottoms from the absorber, now enriched with C_3 and C_4 fractions, is boosted by the rich oil pump through heat exchangers (not shown), and through the convection bank and one side of a double-end Alcorn furnace. Here the heavy naphtha is vaporized and the vapors are superheated to approximately 1030 deg. F. Meanwhile, the cycle gas, containing C_3 and C_4 fractions from the gasoline stabilizer at the far end of the unit, is passing through the gas pyrolysis coil at the other side of the double-end Alcorn furnace, where it acquired a temperature of about 1250 deg. F. On issuing from their respective sides of the furnace the superheated vapors and the cycle gas are mixed in a five-inch transfer line; this mixing is in proportions that give a temperature of about 1070 deg. The transfer line delivers the mixture, still at 150-200 lbs. pressure, to the reaction chamber (or soaker) which is an upright, internally insulated welded steel vessel. The transfer line ends as an open pipe inside and near the top of the chamber; the vapors pass down and out into the scrubber-fractionator. Time of passage through the reaction chamber is two minutes and at the exit from the chamber the temperature has dropped to about 1000 deg. F. The processes that go on within the reaction chamber are undoubtedly very complex and include thermal cracking in the sense of splitting large oil molecules into small ones, with accompanying polymerization, isomerization, dehydrogenation and hydrogenation, and alkylation; in the latter phase a portion of the C_3 and C_4 fractions that were introduced with the rich stabilizer gases are fixed and retained in the final product thus saving desirable values.

Near the bottom of the scrubber the vapors are quenched to about 750 deg. F. by cooled fuel oil recycled from the fuel oil bottoms. The scrubber also furnishes another closed cycle (not shown) for preheating the cycle gas and for reboiling the gasoline in the stabilizer. In another cycle part of the liquid product of the reflux accumulator is returned to the top of the fractionator for temperature (end point) control. The overhead from the fractionator leaves at a temperature of about 375 deg. F. On its way to the reflux accumulator it receives an injection of uncondensed gases from the topping stills. These gases contain values which ordinarily are lost by a topping plant. These values amount to 1 to 3 percent of the due yield of straight run gasoline (depending on the supply and temperature of the condenser water). The recovery of these values and the pyrolysis of the C_3's and C_4's contained therein is an important factor in the economy of the North Tonawanda TVP unit. Farther along on the way from the fractionator the stream receives an addition of light naphtha for blending purposes. The rest of the unit is a conventional stabilizer system which delivers stabilized gasoline and an overhead stream of rich gas, which goes back through the cycle-gas side of the double-end furnace, traverses the reaction chamber-fractionator circuit, and is finally discharged from the absorption tower with not more than 13 percent of C_3 and heavier gases, nine-tenths of which is C_3. Analyses of the entering materials and of the products from the reformer are given in the accompanying Table 1.

The North Tonawanda TVP reforming unit was built by the Alcorn Combustion Company in five months from signing of the contract to

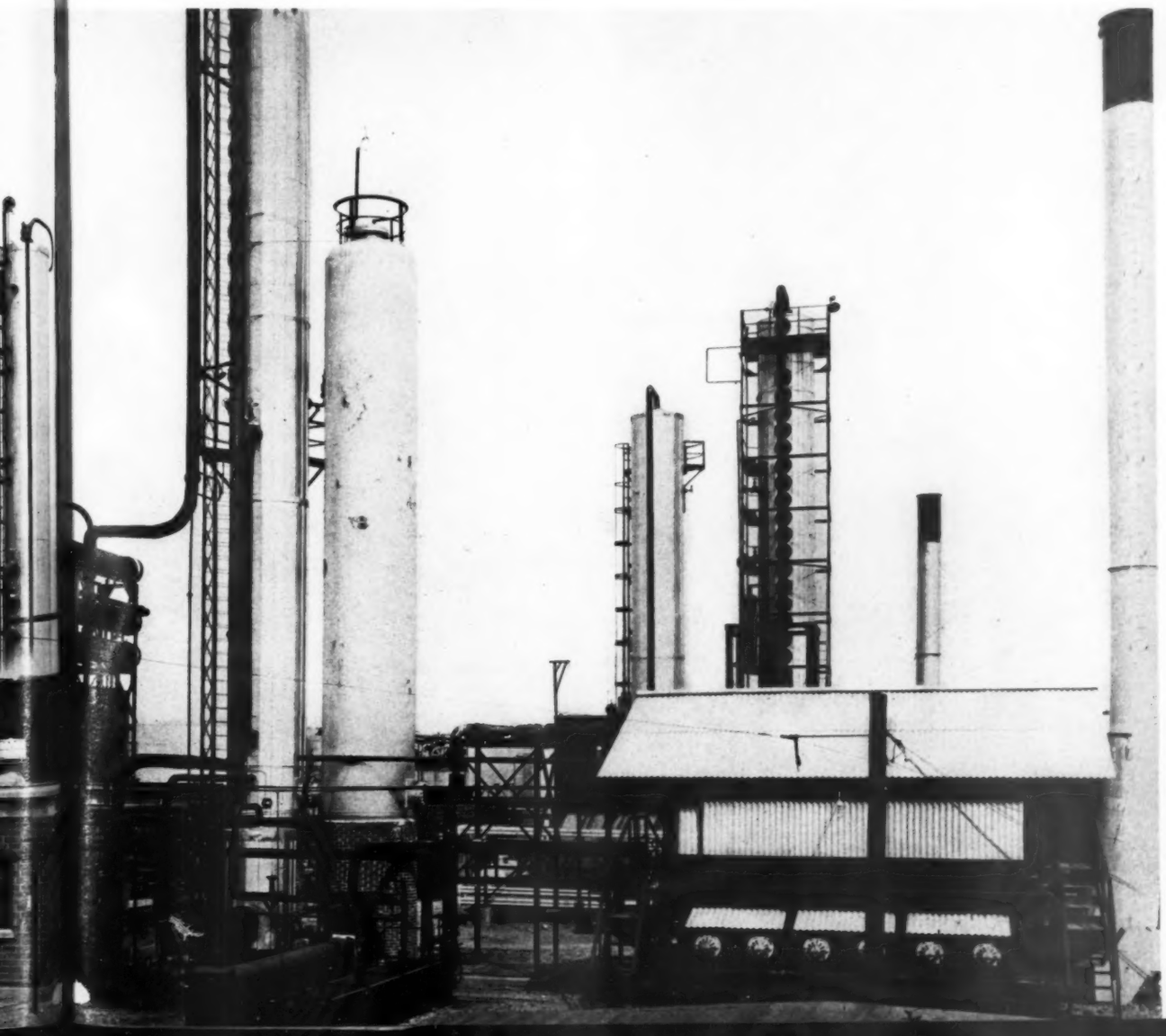


ge of Commercial Application

the first day of operation. The designed capacity was for handling 1,200 bbl. of heavy and 400 bbl. of light naphtha a day, but in regular operation has since reached 1,400 and 800 bbl. respectively. The initial run was 38.5 days; operations were then interrupted in order to tie in an additional tower to the topping still. During this and succeeding runs the unit has functioned smoothly and the performance has exceeded specifications. The plant was contracted under a guarantee to effect a 90 percent conversion into a gasoline with a maximum Reid vapor pressure of nine, a maximum end-point of 410 deg. F., and a minimum octane number of 73.8 ('39 R). The actual conversion was more than 91 (net yield of treated product figured back to total naphtha feed, the Reid Vapor Pressure was 9.3 lbs., the end-point was 401 deg. F., and the octane number was 75.0, which could be raised 7.5 points by 1 cc. of tetraethyl lead. The total cost of the plant is given as approximately $100 per bbl. of heavy naphtha reforming capacity. The installation is operated by one man per shift. No operating difficulties have arisen. In particular, coking troubles that affected the process in the earlier stages of its development have been overcome by the well studied technological control applied to the time-temperature relationships in the reaction.

Besides the operations at North Tonawanda a variety of data are available from operations of a semi-commercial TVP unit. As an illustration of the extent of this work some of these data are shown in Table 4. In these experiments a full range gas distillate from gas recycling operations on the Gulf Coast was pre-distilled to give 50 percent light naphtha, which was charged without vapor loss into the stabilizer of the reforming unit. The 50 percent heavy naphtha was charged by way of the absorber to the reforming heater. It will be observed that the liquid volume yield of gasoline from the added gasses is in excess of 50 percent. Considering the endpoint of the whole distillate the yield, even without the added gases, is worthy of note. Attention may be called to the lead susceptibility of the produced gasoline. Additional work has been done on reforming simultaneously with pyrolysis of the C_3 fraction, in which liquid volume yields of 25 percent of 100 octane gasoline are said to have been obtained.

The TVP process at North Tonawanda is at present confined to the reforming of naphthas and other vaporizable petroleum products, but a form of the new TVP process for application to a reduced crude has been worked out by the Petroleum Conversion Corporation in its semi-commercial plant at Bayway, N. J., and is said to be ready for commercial use. As may be seen from the simplified flow sheet the new TVP cracking system differs from the TVP reforming system chiefly by the inclusion of a vaporizing furnace for the reduced crude. The charge first passes the absorbing tower counter-currently against the rich gases from the reflux accumulator behind the scrubber-fractionator. It then passes through the vaporizing furnace and enters a flash drum. The vapors from this drum pass through one side of a double-end superheater, and are then mixed with heated cycle-gas from the gasoline stabilizer accumulator that has passed through the convection bank and the other side of the same furnace. The mixture of vapor and gas goes through the reaction chamber and scrubber-fractionator in much the same manner as in the naphtha reforming unit. As this new system has not yet been commercialized, no full-scale



Frontier Fuel Oil Corporation's refinery operating on the True Vapor Phase system at North Tonawanda, N. Y. has been on stream long enough to furnish six month's data as to yields and costs.

TABLE I

Laboratory Inspections on Charge and Products

	CHARGE			PRODUCTS		
	Heavy Naphtha	Light Naphtha	Crude Gas	Treated Gasoline	Product Gas	Tar
Gravity, Deg. API	52.0	94.9	...	61.5	...	6.7
Sp. Gr. (Air, 1)	...	...	1.68	...	0.79	...
ASTIM Dist:						
I.B.P. Deg.F.	190	75	...	85	...	...
10 percent	230	93	...	123	...	...
30 percent	257	116	...	180	...	...
50 percent	281	135	...	220	...	...
90 percent	368	...	...	360	...	...
F.B.P. Deg.F.	420	220	...	401	...	...
Gum, Cu. Dish, Mg./100 c.c.	...	...	...	3	...	...
Induction period, Min.	...	...	...	300	...	...
Bromine Number	...	...	...	27	...	...
Sulphur, Wt. percent	0.05	...	...	0.03	...	...
Reid vapor pressure	...	...	...	9.3	...	...
B.S. & W., Vol. percent	...	...	...	...	...	0.3
Visc., furol, 122 Deg.F., Sec.	...	...	...	...	...	31
Octane Numbers '39 Res.:						
Clear	38.0	72.0	...	75.0	...	...
With 1 c.c. T.E.L./Gal.	...	...	...	82.5	...	...
With 2 c.c. T.E.L./Gal.	...	...	...	86.0	...	...
Low Temp. Analyses:						
Hydrogen, Wt., percent	...	...	...	...	0.4	...
Methane	...	...	2.5	...	31.0	...
Ethene	...	...	...	...	19.0	...
Ethane	...	0.7	4.2	...	36.7	...
Propene	...	...	...	...	11.4	...
Propane	...	2.1	32.0	...		...
Butenes	...	...	...	2.5	1.5	...
Butanes	...	12.9	55.5	4.0		...
C 5's	...	17.3	5.8	5.5	...	...
C 6's and heavier	...	67.0	...	88.0	...	...

operating data are available at the present time. From results at Tonawanda it would appear that the TVP process has come through the difficulties of the development stage and has taken a definite place among the resources of the petroleum technologist, alongside of other well known and approved processes; where it will best fit in will depend on the circumstances that confront the individual refiner. While the principle of true vapor phase reaction is applicable to any petroleum product that can be vaporized, it would seem to have a particular appeal to small refineries that cannot afford the high investment costs of the modern catalytic cracking and reforming processes. With a TVP reforming unit it seems that the small refinery can obtain a proper balance of its products, solve its octane problem, and need lose nothing but "make gas" that contains no values worth mentioning, except fuel value. There are few engineering or constructional difficulties. No special alloys are required except chromium-silicon steel for the radiant tubes of the furnace and 4-6 chrome steel for the convection bank and the transfer line.

TABLE II

Charge to TVP Unit	Liquid Vol. %
Light Naphtha	28.2
Heavy Naphtha	71.8
Total Naphtha Feed	100.0
Topping Still Gases	1.9*
Products (Basis Naphtha Feed)	
Treated Gasoline	91.2
Residuum	0.9
Product Gas	9.4**
Loss (Treating)	0.4
Temperatures (Deg.F.):	
Outlet superheater coil	1030
Outlet cycle gas coil	1230
Inlet reaction chamber	1070
Outlet reaction chamber	950
Scrubber bottom oil	600
Fractionator top vapor	385
Pressures (lbs./Sq. In Ga.):	
Reaction chamber	180
Fractionator	170
Stabilizer	225
Absorber	150

* 58.3 M Cu. Ft./Day

**627.2 M C. Ft./Day

TABLE III

Utility Consumption in TVP

Fuel Fired (Gross)	16,500,000 B.t.u./hr.
Steam (180 lbs. to 15 lbs. exh.)	1.135 lbs./hr.
Cooling water (85 Deg.F.)	560 Gals./Min.
Electric power	53 kw./hr.
Treating & inhibiting/bbl. gasoline	1.9 cents

The rest is simple welded steel equipment that can be put together by any shop that is equipped to roll ½" to ¾" steel plate. In view of the present and possible future demand for petroleum by-products created by national defense requirements, the true vapor phase process has some interesting implications. The question of a synthetic rubber substitute looms ahead, and this raises the problem of a supply of butadiene. Since the heating method in TVP, wherein highly heated gases are mixed, permits almost instantaneous temperature increase to the desired reaction temperature, the process lends itself well to the establishing of the extremely high temperature-short time reaction essential to the production of butadiene thermally from oils. As an example, 38.9 deg. API Pennsylvania gas oil having 465 deg. F. IBP and 700 deg. F. FBP was processed at approximately 1400 deg. F. at an extremely short time interval to yield the following:

	Wt. % Basis Feed
Hydrogen	0.13
Methane	9.07
Ethene	13.17
Ethane	7.38
Propene	13.62
Propane	1.79
Butadiene	5.03
Butenes	9.21
Butanes	0.70
Pentadienes	1.96
Pentenes	4.38
Pentanes	2.02
C_6 and heavier	6.07
Residue (10 deg. API)	22.17
Losses	3.30

On the basis of the yields obtained in this operation it is interesting to note that a 10,000 bbl. per day unit would produce approximately 25,000 tons per year of butadiene which could be recovered and purified by established methods to be used for synthetic rubber. The flexibility of control of reaction time and temperature which permits establishing conditions favorable to butadiene formation also permits of setting a long-

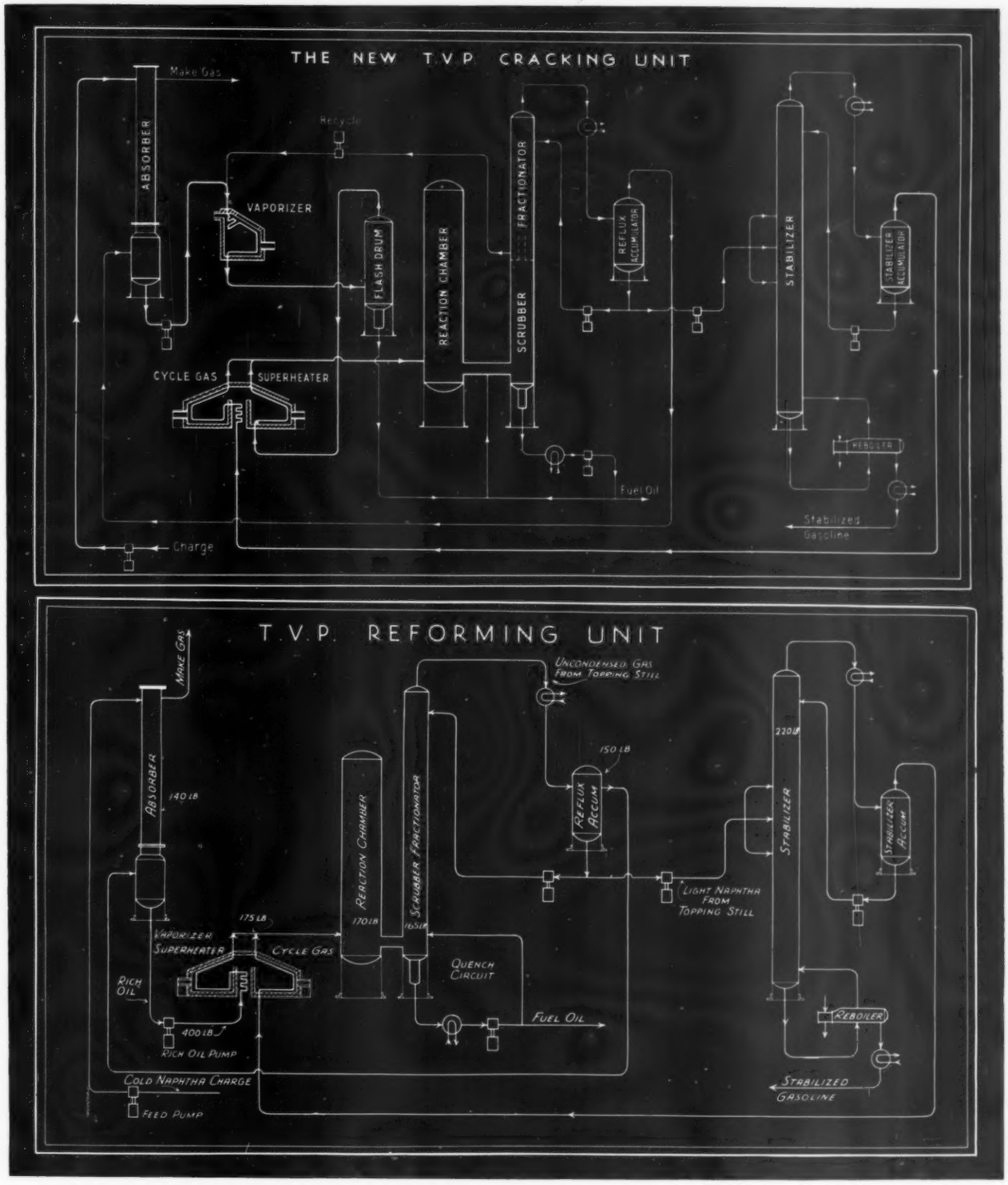
TABLE IV

Yield and Operating Data

Reforming Gulf Coast Gas Distillate

CHARGE TO TVP UNIT	VOLUME PERCENT			
Total Gas Distillate	100.0	100.0	100.0	100.0
C 4's (50% Olefin)	...	7.5	...	9.1
PRODUCTS				
Gasoline	90.4	94.5	83.4	88.4
Residue	4.5	3.9	4.3	3.4
Gas	5.1	9.1	12.3	17.3
Total Products	100.0	107.5	100.0	109.1
OPERATING CONDITIONS				
PRESSURES Lbs. Ga.				
Reactor	150	150	150	150
Fractionator	145	145	145	145
Absorber	140	140	140	140
Stabilizer	200	205	200	200
TEMPERATURES Deg. F.				
Gases	1200	1255	1200	1240
Vapors	1005	950	1115	1070
Reactor In	1050	1050	1120	1120
Reactor Out	930	960	970	980
LABORATORY INSPECTIONS				
Gas Distillate Feed				
Gravity, Deg. API	64.5			
Reid Vapor Pressure	9.6			
ASTM Octane Number	59.8			
Research Octane Number	59.9			

ASTIM Distil'ation:				
IBP Deg.F.	93			
20%	170			
50	218			
70	273			
90	388			
95	460			
FBP	493			
PRODUCT GASOLINE				
Gravity, Deg. API	67.2	66.0	66.5	66.1
Reid Vapor Pressure	9.9	10.5	9.2	9.8
ASTM Octane No.	68.0	69.4	71.4	72.9
1 CC TEL	78.7	79.8	81.6	82.0
2 CC TEL	81.8	82.2	83.2	83.2
Research Octane No.	71.8	72.7	77.5	78.8
1 CC TEL	81.8	84.0	85.9	86.5
2 CC TEL	84.7	86.8	89.3	90.0
ASTM Distillation:				
IBP Deg. F.	86	91	95	92
20%	138	135	130	134
50	191	190	181	184
70	234	237	218	224
90	312	330	302	310
FBP	383	393	382	389
Product Gas				
Sp. Gr. (Air 1)	0.77	0.82	0.83	0.82
Residuum				
Gravity, Deg. API	34.8	30.2	21.0	18.4
Vis at 100 Univ., Sec.	35	41	46	56



er time factor at slightly lower temperatures for the production of aromatics, particularly toluene, much needed in war and industry today. While all cracked gasolines, and even straight-run gasolines to a lesser extent, contain small quantities of toluene, some of the commercial products from the TVP process will contain as much as 2 to 4 percent. Results of semi-commercial operations are shown below:

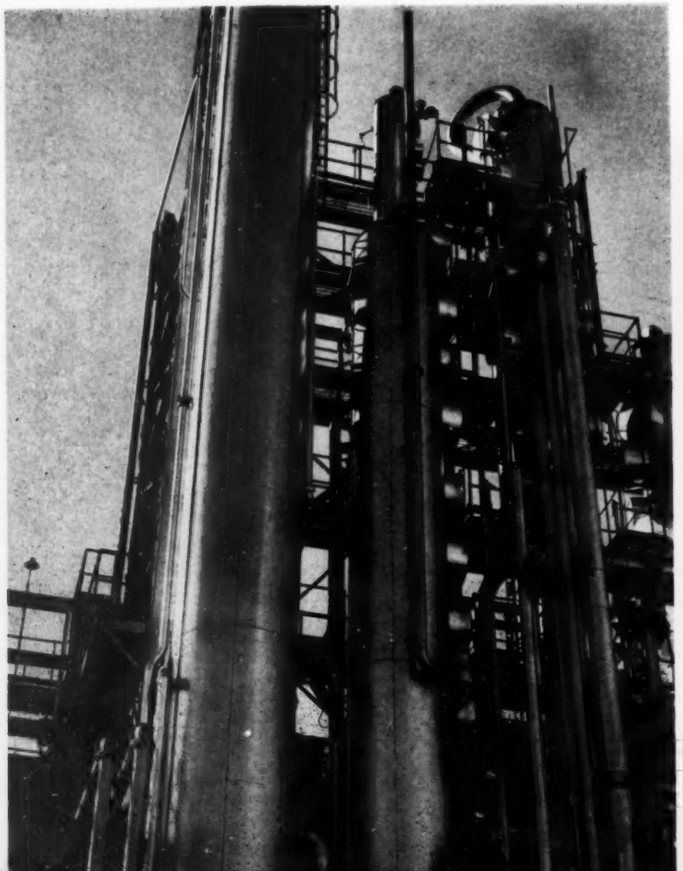
Charge	Type of Operation	Cracking Temp.	Toluene Basis Charge Vol. %	Yield Basis Distillate %
E. Tex Gasoil	Single Pass	1110 deg. F	3.28	9.10
200-400 Ill. Naphtha	Reforming	1120 deg. F	3.65	6.30

Since conditions suitable for maximum aromatic formation are not suitable for maximum production of marketable motor fuel it is necessary to increase the reaction severity considerably to increase aromatic formation. This, of course, results in a lower yield of distillate but increases toluene concentration.

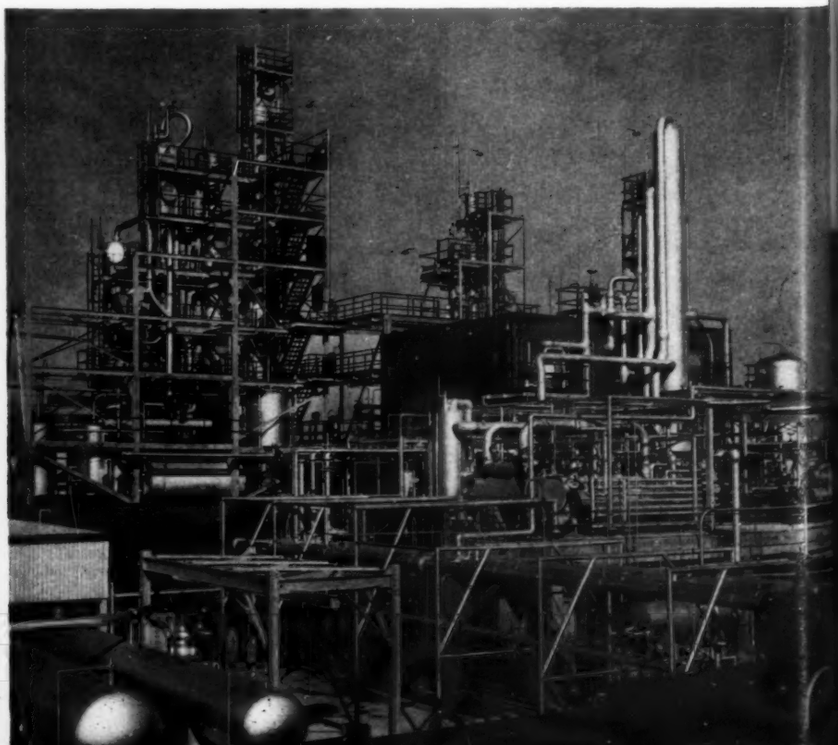
Airview of Continental Oil Company's general offices and major refinery at Ponca City, Oklahoma. The new solvent treating plants lie between the office building and the first group of storage tanks.

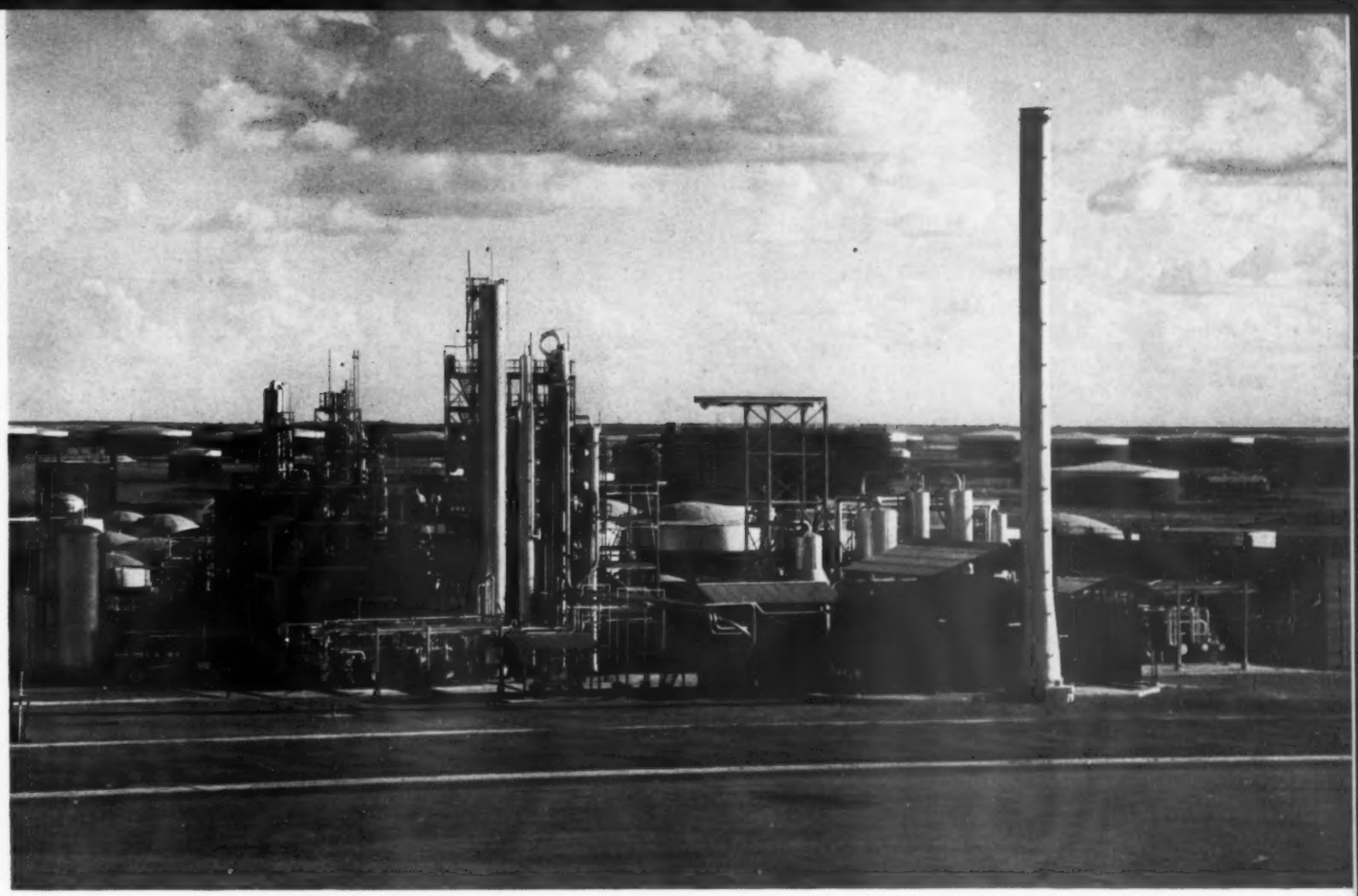
CONTINENTAL COMPLETE

Close up view of treating towers on the furfural solvent treating plant.



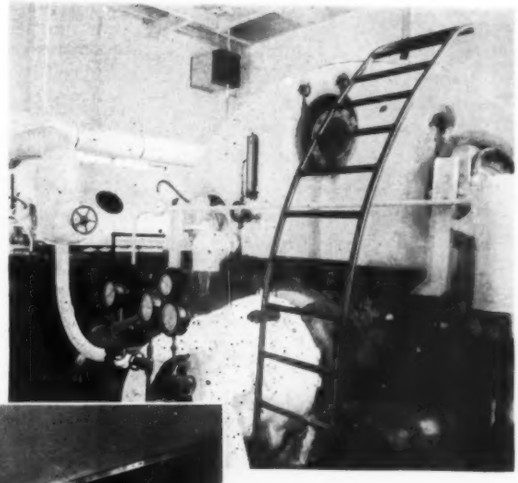
Contacting and exchanger equipment in the Duo-Sol, furfural, and methyl ethyl ketone plants.





The solvent treating plant as seen from Continental's general office building. In the background is part of the compay's 10,-000,000 bbl. tank farm and in the distance may be seen the tops of producing wells in the South Ponca field.

TE Solvent Refining Units at Ponca City Refinery



Right, rotary filters in the methyl ethyl ketone plant where raffinate from the furfural plant is dewaxed.

Left, control room, nerve center of the entire solvent treating cycle, where every step of the three processes is checked and recorded.

CONTINENTAL OIL COMPANY recently completed Duo-Sol, furfural and methyl ethyl ketone units for solvent refining of lubricating oils at the company's Ponca City, Oklahoma refinery, the largest of Continental's nine manufacturing plants and the only one to produce the company's wide range of motor and industrial oils.

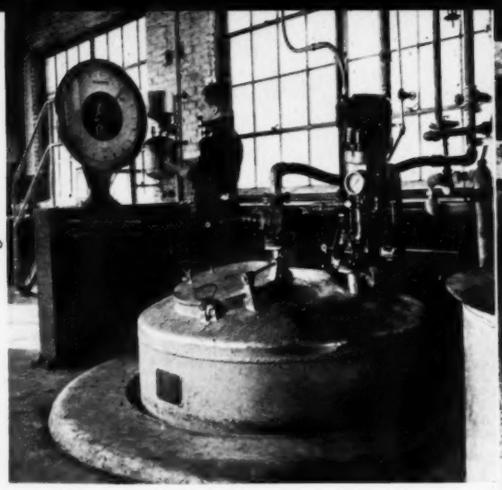
The three new processes were integrated with the centrifuge dewaxing process, used to dewax residue oils, modernized to utilize hexane as the solvent, and also with the Bari-Sol process, which has been in operation in the plant for the past couple of years. About 1,600 bbl. of heavy vacuum-distilled lubricating oil bottoms are charged into the Duo-Sol plant daily, where it contacted with the phenol-cresol blend, Selecto, and with liquid propane. Seven horizontal drums perform the contacting and separation processes, carried out under a pressure of 300 lbs. per sq. in. The extract solution is then processed to recover the solvent, while the oil raffinate is dewaxed in the hexane dewaxing plant. About 1,200 bbl. of light wax distillate, with a viscosity of 75 to 80 at 100 deg. is charged daily into the furfural plant, where it is solvent treated and rerun to make a 180 viscosity motor oil base. The raffinate here is sent to the M.E.K. unit for dewaxing. The M.E.K. plant, which is conventional in operation, handles from 750 to 900 bbl. of raffinate daily, depending on its grade. From the M.E.K. filters the charging stock is put through solvent-recovery units, and the crude-scale wax sent to the sweat pans, where a 130-m.p. wax is produced.

At present the new units are operating at capacity manufacturing the company's newest motor oil, recently introduced to the marketing field under the name, "Nth," symbolizing the "nth" degree of perfection. Also employed in the manufacture of this lubricant are two additives: methyl dischlorostearate, for greater film strength; and thialkene, a sulfonated olefin developed by Continental chemists to reduce oxidation tendencies in lubricating oil.

SYNTHETIC RUBBER Faces Bright Future

By Dr. Waldo L. Semon

New Fields of Industrial Usefulness for Synthetic Rubber Without Replacing the Natural Product in its Own Sphere.



Above left, view of a polymerizing vat in the Akron plant of Hycar Chemical Company straight-line synthetic rubber production unit. Above right, Dr. Waldo L. Semon inspecting a curd of Ameripol which is used in the manufacture of the first synthetic rubber automobile tires to reach the open market. Dr. Semon is a recognized authority on synthetic rubber. For a number of years he has been in charge of investigation in this field for the B. F. Goodrich Company and he conducted the research that led to the development of Ameripol through polymerization of butadiene. Dr. Semon is Vice President of the Hycar Company jointly owned by the B. F. Goodrich Company and Phillips Petroleum Company.

SYNTHETIC rubber's place in industry's future "design for living" will grow out of its chemical compatability with two prime industrial materials, petroleum and rubber, which cannot abide each other but get along with the man-made substance very well. This perspective becomes clear when we realize that scientists are projecting their picture of the future more and more in terms of petroleum, not merely as the fuel for internal combustion engines but also as the source of the versatile hydro-carbon molecule which modern industrial science can transmute into many valuable raw materials. These materials derived from petroleum are going to establish themselves firmly in our industrial pattern in the next few years. But for the development of synthetic rubber, this increased volume of petroleum products could be handled in flexible hose and with other rubber applications only with difficulty, because contact with petroleum causes natural rubber to swell and disintegrate. Thus synthetic rubber will play a dominant role as the "age of petroleum" expands because it not only has the elasticity and other indispensible properties of natural rubber, but being itself derived from petroleum resists the action of oil and is therefore used successfully in connection with it. That is why I believe the future of synthetic rubber does not depend upon the replacement of natural rubber but will develop new uses.

Those who have scanned the industrial horizon anticipate that the specific properties of synthetic rubber will open new fields for its use at such a rate that its ability to compete with natural rubber at the latter's lower production cost will be a secondary feature when weighed against the special services which the man-made product can render. The cost advantage of natural rubber, leading import of the United States both in tonnage and dollar value, may well be outweighed by the fact that synthetic rubber gives superior service in such applications as filling station hose, conveyor belting, printing plates and fuel feed systems for aircraft, Diesel and almost every type of internal combustion engine. The field for products of this type is rapidly expanding and for several years a growing line of synthetic rubber appliances has been developing. In addition to its fortunate relationship with petroleum and hydrocarbon products, man-made rubber is virtually unaffected by many modern industrial solvents and is thus a prime tool in processes involving such chemical agents.

The versatility of synthetic rubber is illustrated by results of a year of intensive testing in our Akron laboratories and in actual service. We found that synthetic rubber excels natural rubber in four important service characteristics, equals it in six and is only slightly below natural standards in three. The tests showed that Ameripol, which is being used in the first synthetic rubber automobile tires to reach the open market, excels natural rubber in its resistance to oil, oxidation, aging and heat. It equals nature's product in range of hardness, elongation, tensile strength, permanent set and in resistance to abrasion, acids and alkalies. It is only slightly below natural standards in elasticity, tear resistance and reaction to sub-freezing temperatures, and even these can be remedied by skillful compounding. There seems little question that synthetic rubber can be a success in developing an entirely new field of industrial utility without disturbing the time-honored position of natural rubber in hundreds of fields where it is entirely adequate as a material. We should not be impatient, however. We have spent fifteen years at B. F. Goodrich Company developing a synthetic rubber capable of replacing the natural product for practically all its essential uses, including tires. But an indication of what we can expect from this man-made product is found in the service reports from thousands of motorists who have found that synthetic rubber tires measure up to the same standards of performance and quality as natural rubber casings.

The pioneering experience gained in this development has led the company to expand its privately financed synthetic rubber production to 7,000 long tons a year. This capacity, coupled with a 10,000-ton plant to be constructed with government funds at Louisville, Kentucky, will provide the company's synthetic rubber affiliate, Hycar Chemical Company, with a capacity four times that of the entire country last year. The production capacity of Hycar alone, namely the 17,000 tons expected by the end of 1942, compares with the capacity of 20,000 tons a year which the Department of Commerce reports that Nazi Germany had attained at the outset of the war after years of urgent effort. The funds being expended on synthetic rubber are not being scattered like chaff in the wind. In the next few years I expect to see synthetic rubber fit itself into the industrial pattern which has become so familiar since the turn of the century—the development of materials and mechanisms which cost more but more than offset that greater cost by rendering unique services that soon become indispensable to modern industrial progress.

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WORLD PETROLEUM ABSTRACTS

Summaries of the Most Important Articles as Published in the Oil Press of the World Dealing with Technical and Economic Aspects of the Petroleum Industry — Edited by Dr. O. W. Willcox.

GEOLOGY

Micropaleontology — Past and Present. — Carey Croneis, in Bulletin AMERICAN ASSOCIATION PETROLEUM GEOLOGISTS, Vol. 25 (1941), No. 7, pp. 1208-1255. This paper outlines the history of the science of micropaleontology, which is the science of fossils that can hardly be seen by the unaided eye.

It is pointed out that heretofore the micropaleontologists have been concerned almost exclusively with one kind of microfossil—the *foramenifera.* They have lately awakened to the fact that there are other small fossils that have or may be found to have diagnostic value. These are *ostracodes, conodonts, bryozoans, radiolaria,* and others. It has transpired in the past that important geological information has been overlooked by microscopists who have been trained only to look for *foramenifera,* whereas other microscopists who had acquired information about *conodonts* and *scolecodonts* were able to identify the formations in question by reason of their more extensive knowledge.

This is now in the way of being remedied. The study of microfossils is being put on a broader basis in the colleges that are now teaching the subject. The course of study is being enlarged to take in all forms of fossils that would naturally come within the field of a microscope. As a result, the resources of the petroleum geologist should be considerably enlarged.

The Future of Geophysics—W. T. Born, in Bulletin AMERICAN ASSOCIATION PETROLEUM GEOLOGISTS, Vol. 25 (1941), No. 7, pp. 1256-1263.

It is considered to be an obvious necessity that the technique of oil exploration must continue to improve if the future rate of discovery is to be kept on a par with that of the past.

The reason for the necessity of improving this technique lies in the fact that most if not all the easy work has been done. The methods of the past and present have been sufficiently precise to discover large and easily defined structures. What remains now are mostly structures of low relief, and small structural traps in large fields that have been worked over by methods that aimed to cover as much ground as possible at the least expense. This ground will now have to be gone over again with a fine toothed comb, as it were, in an effort to glean what has been overlooked. This resurveying of old areas has proved to be very successful in Oklahoma.

The author calls attention to the fact that the average depth to which Gulf Coast area has been geophysically surveyed is less than the depth of many wells now being drilled. This, the author thinks, is certainly a situation which should be corrected, which means that it is about time for this area to be seismographed once again to map deeper horizons.

Besides looking for structures that have escaped notice in old territory, the geophysicists will have to sharpen their tools for the discovery of stratigraphic traps. There is a prevailing notion that such traps are not associated with structure. But various facts are cited to show that this is not always the case. The Coalinga fields in California are examples of traps or pinch-outs, the existence of which was suspected from geological evidence and confirmed by careful geophysical work which located the nose.

In conclusion, it is largely a question of improved instrumentation and technique. There is still more work for the principal techniques that have been successfully used in the past, but it appears that from henceforth this work must be done with greater precision.

DRILLING

Effect of Calcium Chloride in Oil Well Cements —F. N. Alquist and H. H. Miller in OIL & GAS JOURNAL, Vol. 40 (1941), No. 10, pp. 42, 45, 49-50.

Most dam builders and other contractors in ordinary civil engineering work understand the uses of calcium chloride, but the requirements placed on oil well cements are different, and it has seemed necessary to write this article because the subject is apparently not too well understood by engineers in charge of oil well operation.

The chief point of the matter is that present practice

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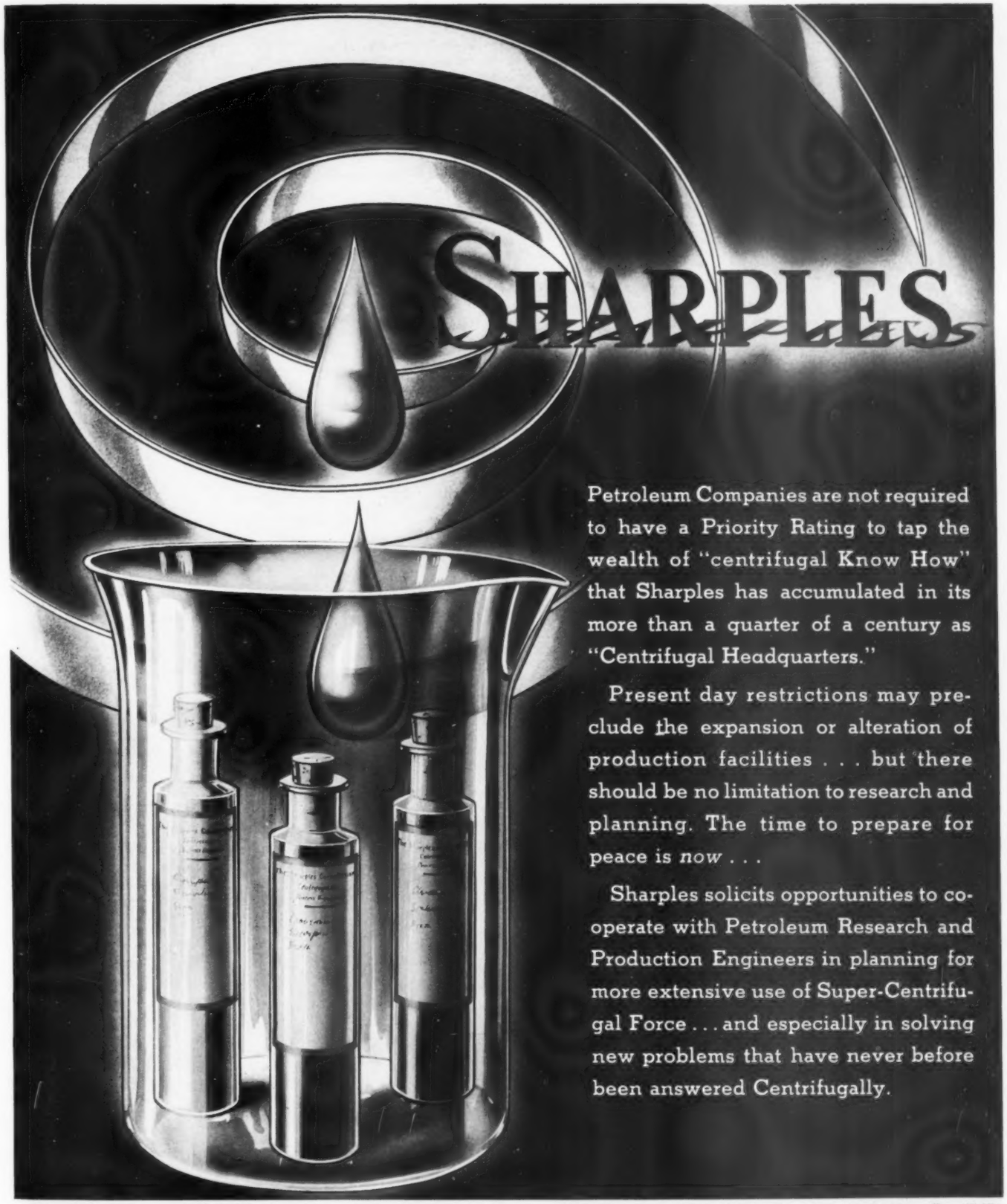

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calls for the use either of relatively expensive oil-well cements or "high early" cement, whereas the technique employing the addition of calcium chloride is simple and allows the relatively cheap ordinary portland cement to be used instead. Hence the oil-well engineer who is familiar with the effects of calcium chloride as they are described by the authors can readily make his own cost comparisons. The points which speak for the use of this very common and cheap chemical are listed as follows: Regular portland cement with 2 or 3 per cent calcium chloride added offers a saving of time and money to oil operators in cementing surface and low-temperature strings.

The final setting time of regular portland cement is reduced approximately 30 per cent by the addition of 2 to 3 per cent calcium chloride.

Quantities up to 4 per cent of calcium chloride admixed with portland cement require the same or slightly less water-cement ratio for standard fluidity.

The use of calcium chloride in both "high early" and portland cement increases the early strength. The portland cement and calcium chloride admixture acquired a strength at 8 hours that was practically equal to that of "high early" and calcium chloride and more than twice the strength of neat "high early" at 8 hours. This held true whether tested at 60° or 150° F.

Two and three per cent of calcium chloride reduce the thickening time of regular portland and high early cement approximately 50 and 33.5 per cent, respectively.

The quantity of heat generated during the setting of regular portland cement with calcium chloride is no greater than when the calcium chloride is omitted. The heat is generated within the first 24 hours, parallel with the increase of strength.

The setting and thickening times of regular portland cement are greatly accelerated by increased temperature regardless of whether or not calcium chloride is used. Three per cent calcium chloride mixed with regular portland cement reaches approximately 1,000 pounds per square inch in 12 hours at 68 degrees F.

Gel-Cements and Their Application in Well Cementing Operations—Cedric Willson, before A. P. I. DIVISION OF PRODUCTION, Spring meeting, Amarillo, March, 1941.

Gel-cement is portland cement mixed with bentonite. Bentonite, or colloidal clay, has been used in admixture with cement and water in oil well cementing operations for about 10 years. In the opinions of various operators the results have ranged from very successful to unsuccessful, and this use of bentonite is still a controversial question. The author, a cement expert, makes a contribution toward clarification of the matter.

In general the addition of bentonite to portland cement will: (1) Tend to hold cement in suspension until initial set occurs. (2) Increase its plasticity and "viscosity." (3) Reduce the loss of free water when slurry under pressure contacts porous or permeable bodies. (4) Impart a thixotropic property.

These four things are all that can be accomplished by the use of gel-cement and any advantage it may have in oil well cementing operations must be based on one or more of them.

One condition for success is that bentonite and cement should be well mixed in proportions suited to the job. The best way to get a proper mix is to have the mixing done at the cement factory.

Perhaps the main function of bentonite in these mixes is to prevent sedimentation of the cement until the cement has set.

The proper percentage of bentonite for the make-up of gel-cement depends on the purpose. When it is desired to prevent sedimentation in a high water-cement ratio slurry, strength tests indicate that 4% is probably the upper safe limit. With a greater percentage of bentonite, strengths are dangerously low and the slurry is undoubtedly very permeable. The best method would seem to be a selection of the strength desired which will automatically set the percentage of bentonite required to eliminate sedimentation for that particular water-cement ratio. When it is desired to build up the "viscosity" or plasticity of a certain water-cement ratio slurry, the percentage of bentonite will be limited by the decrease in pumpability and setting time. Ordinarily a 2% gel-cement will provide as plastic a slurry as the pumps will handle and, with a low water cement ratio, the limit may be reached with 1% or 1.5% bentonite.

Recent Equipment for Paraffin Removal, Perforation Cleaning, and Well Completion—Benton Turner, before A. P. I., DIVISION OF PRODUCTION, Spring meeting, Los Angeles, March, 1941.

Four new tools, all still largely in the development stage, have been selected as those which offer the greatest promise of improving production technique and reducing operating costs. They are as follows:

1. An electrical heating process for intermittently removing paraffin accumulations from the tubing of pumping wells.

2. A perforation washer that enables the operator to test individually each row of perforations around the casing and offers a method of injecting chemical that has not been previously mixed with the fluid in the well through the perforations.

3. A well cleaning process in which oil is driven through the clogged perforations of the liner by

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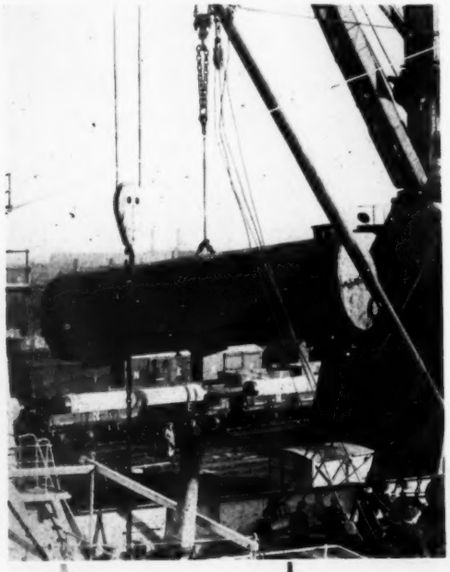

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the forces released from an exploding gas torpedo.

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Because of the newness of these tools, data on their use are limited. Use of the electrical heating equipment in its present form was initiated about twelve months ago. Development work on the perforation washer has been completed within the last four months.

The gas torpedo has been tried in about a dozen wells in California although its use in Texas goes back eighteen months. The gun tester unit has been used commercially in Texas for the past ten months but has yet to be used in California.

Merco Nordstrom to Entertain API

Arrangements have been made by members of the Merco Nordstrom Valve Company executive and engineering staffs to entertain visiting members of the American Petroleum Institute at the Annual Meeting in San Francisco. Entertainment headquarters will be maintained at the Mark Hopkins and Fairmont Hotels and transportation facilities will be provided to take visitors on an inspection tour of the principal Nordstrom Valve manufacturing plant across the Bay in Oakland. Colonel W. F. Rockwell, president of the organization will be on hand to welcome guests and will be assisted by other members of the Merco Nordstrom organization from all parts of the country.

Mud Control as an Aid in Mid-Continent Drilling —E. R. Albert, before A. P. I., DIVISION OF PRODUCTION, Spring meeting, Amarillo, March, 1941.

This paper emphasizes that the most important single characteristic of a good drilling fluid is its ability to build a thin impervious filter cake on the wall of the hole with a minimum of water lost. Such muds are described as low-water-loss muds. Where the water-loss is low the mud cake is thin; and where the water loss is high the mud cake is thick. A thick mud cake is the parent of a host of drilling troubles, which the author catalogs at considerable length.

The main point, then, is to control the mud in the direction of low water loss. A safe practice recommended for normal mid-continent drilling is to carry a 9.8 lb. to 10.2 lb. natural mud; if it is necessary to weight this mud the weighting should be done with colloid materials that will give proper viscosity, filtering rate, and gel strength. By attending to this detail several major companies in Oklahoma have been able to drill up to 10,000 ft. with only surface casing in the hole, where a few years ago they had to put in 3,000 to 6,000 ft. of intermediate casing. Another saving has resulted from ability to drill through pay sections without setting pipe or drilling in with oil, all because of controlled water losses from drilling mud.

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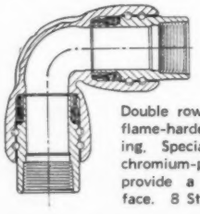

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named) is as effective in stopping voids as other colloids in fresh water.

The paper closes with the statement that since low-water-loss muds are available in both fresh and salt water drilling fluids, neglecting them is to assume an unnecessary hazard.

OPERATION

Gas Well Acidifying in the Texas Panhandle—Gilbert L. Leach, before DIVISION OF PRODUCTION, MID-CONTINENT DISTRICT, Amarillo, March, 1941.

The problem of acidizing wells in the Texas Panhandle presents many complexities, which have required the adoption of a large number of expedients. The varying character of the calcareous zones that need acid treatment put varying requirements on the acid used. In some cases the action of the acid has to be intensified, and in some cases retarded. The acid must furthermore contain wetting agents that enable it to penetrate farther in tight zones, stabilizers to keep dissolved iron and aluminum in solution, and inhibitors to prevent the acid from corroding metal equipment.

In addition to such adjustments of the composition of the acid it is necessary to follow a definite plan for injecting the acid and with-drawing it after it is spent. Each case requires a special study.

Present practice in the Panhandle calls for the use of gas compressors to force the acid as far as possible into the formation before it has become spent. This practice is regarded as having introduced a new era in the acidizing art. It has greatly increased output in many cases. After the acid has been placed in the well pressure is applied by a compressor capable of handling up to 80,000 cu. ft. of gas per hour and of reaching a pressure of 2,500 lbs. per sq. in. This not only forces the acid far back, but when the pressure is released the gas expands and blows back the acid, thus clearing the well in a few minutes. In some cases the entry of the acid into tight zones is promoted by dropping in 80 lbs., more or less, of magnesium metal, which dissolves with much heat; the hot acid is then capable of more effective penetration.

Acidizing to Remove Drilling Mud and to Clean Up Sandstone Formations—Stanley G. Morian, in PETROLEUM ENGINEER, Vol. 12 (1941), No. 7, pp. 67-68; 70.

Acidizing of wells was first used in the petroleum industry for loosening up limestone formations, and it was not long before it was employed to decompose hardened, impervious mud sheaths that might be sealing oil and gas horizons. It seems that this latter circumstance is of a somewhat wider extent than is commonly supposed. Most native clays encountered in drilling contain some bentonite-like materials that may penetrate the porous, permeable pay horizons and cause abnormally low rates of production. It has also transpired that montmorillonite and similar clay minerals occur to an appreciable extent in sand wells. It has also been supposed that oil moving from the sand toward the face of the well carries with it some of this clay material that clogs the pores through which the oil should pass.

In any case, besides an acid that will attack lime carbonate the oil industry has come to need an acid that will attack bentonite and its relatives that impede production in sand wells. The composition of the "mud-acids" that have been developed for the purpose are more or less trade secrets of the acidizing companies, but the point is that these mud acids will dissolve clogging materials which a 15 per cent hydrochloric acid will not touch. They are used not only to clean the mud off the face of a newly completed well, but to rejuvenate old wells that have become clogged with noncarbonate deposits in oil sands. An example is given of a well in East Texas where the permeability of the sand was increased three-fold. It is stated that it is no uncommon thing for a mud acid treatment to increase production from old wells that were pumping 5 bbl. to 100 bbl. a day. As a general hint it is stated that a sand well whose core shows 10 to 20 per cent of bentonite will be a suitable subject for a mud acid treatment.

Acidizing Oil Reservoirs in Sands—P. E. Fitzgerald, J. R. James and Ray L. Austin, in BULLETIN AMERICAN SOCIETY PETROLEUM GEOLOGISTS, Vol. 25 (1941), No. 5, pp. 850-870.

It is well known that treating oil-bearing limestone formations generally increases the rate of oil production by providing a greater free surface for the passage of the oil.

The same idea is being more or less generally applied to oil deposits in sand formations. Although sand itself is not soluble in hydrochloric acid, it has been found that the interstices between the sand grains contain more or less material that can be removed by acid, thus enlarging the sand's porosity and permeability.

In this work the authors studied more than 300 cores taken from more than 80 different oil-producing sands in twelve states; the age of these sands ranged from Ordovician to Miocene. The solubilities of these sands vary from nearly zero (0.01 per cent) to nearly 100 per cent. The average solubility was about 8.5 per cent.

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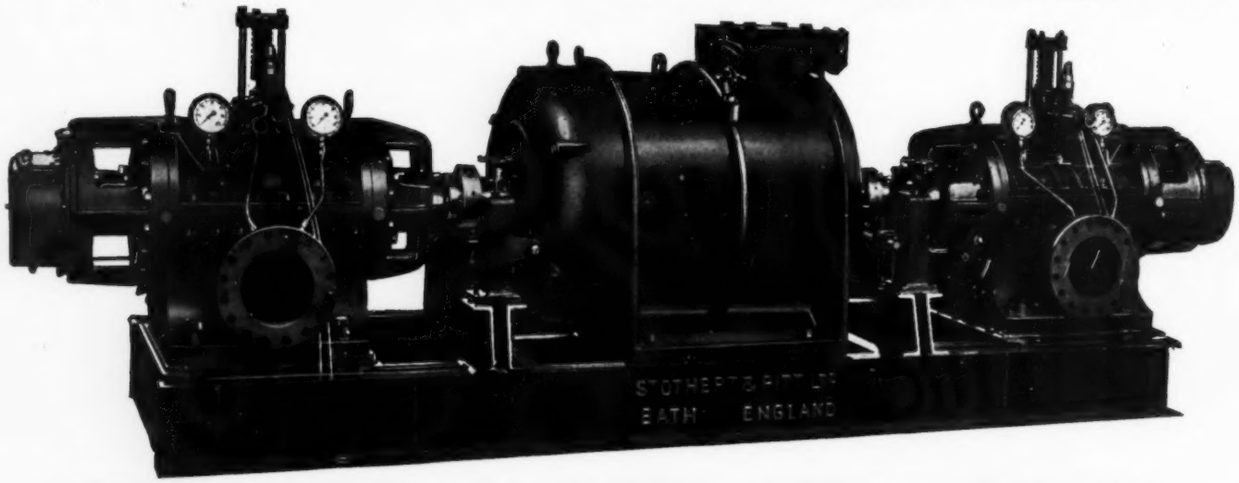

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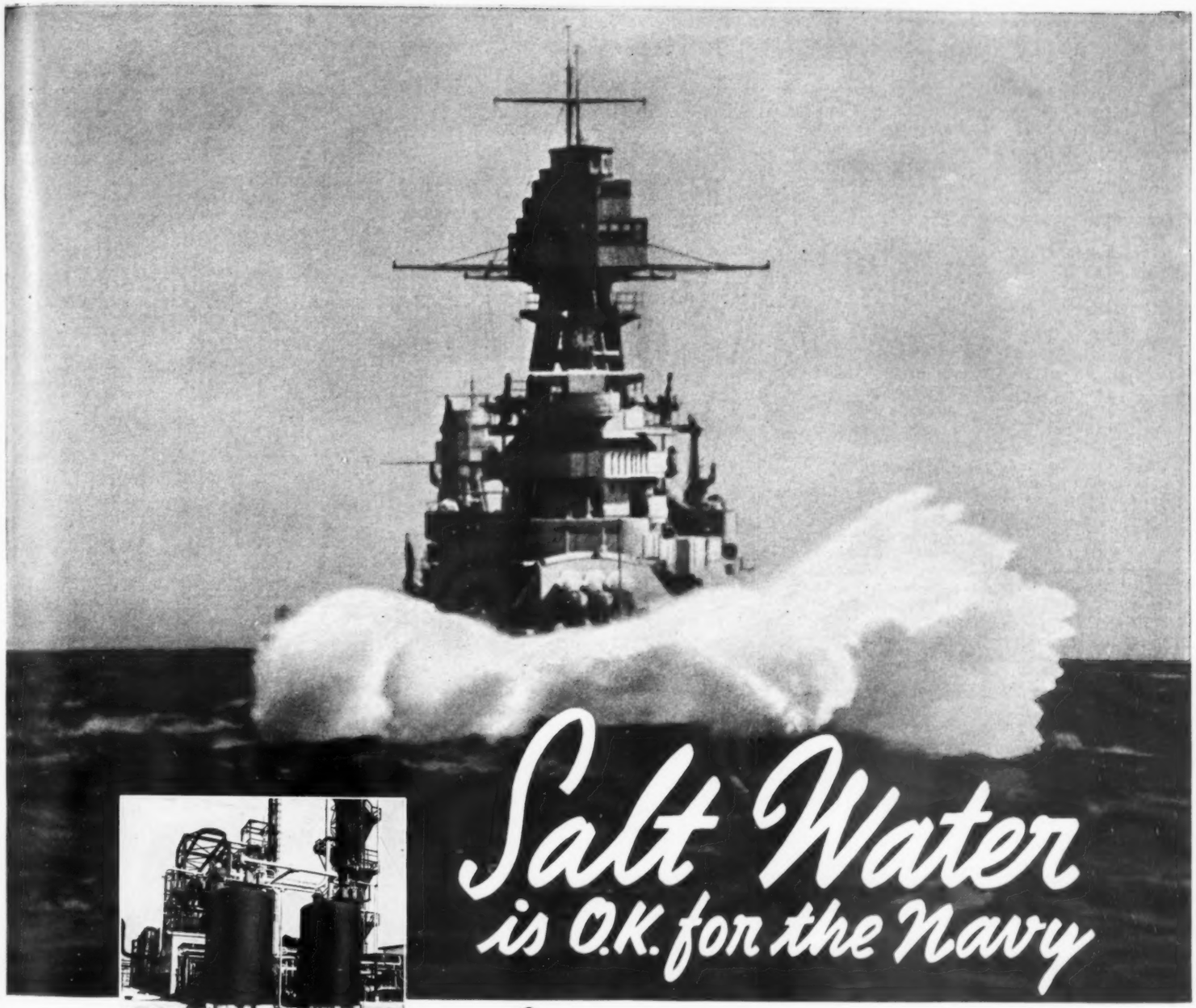

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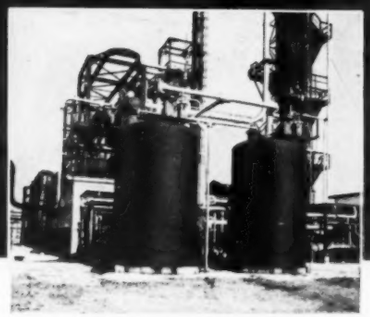

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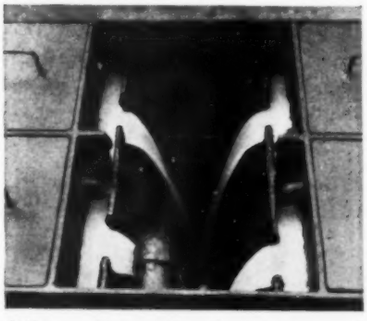

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When the acid solubility of a sand core has been determined the resulting increase in porosity and the presumptive increase in oil production to be expected from acidizing can be calculated from theoretical considerations. But it not seldom happens that the increase in production is much greater than was to be expected. A possible explanation is that the acid has found thin crevices that were easily attacked giving a proportionately much larger free surface.

It has been noted that the crushing strength of acidized sands is sometimes much reduced (but there does not seem to be any evidence that this has resulted in caving in deep wells. Editor).

Besides direct attack by acid, it is mentioned that the acid solubility of a rock sample may be approximated by an X-ray examination which will identify the soluble materials present. This presents the acidizing engineer with an alternative method for getting necessary information.

Production Under Effective Water Drive as a Standard for Conservation Practice—E. De Golyer, in PETROLEUM TECHNOLOGY, Technical Publication, No. 1340; 4 pp. May, 1941.

This paper adopts the standpoint that the problem of good engineering practice and of good conservation practice is that of keeping gas in solution. This can best be done by producing a field as a water-drive field. If someone should say that this is all right where a water-drive is present, the answer is that water-drive is present to a much greater extent than is commonly believed; it is estimated that water-drive great enough to be effective is present in more than 80 per cent of the oil fields of the United States.

If some degree of water-drive is of such common occurrence, why has it not been more commonly recognized? Probably because under the urge for a quick payout most pools have been produced at a rate too high to permit the water-drive to be effective; hence even its presence has not been recognized.

The fact is that, for the reason above mentioned, the great bulk of the oil fields of the United States are being produced as gas-expansion fields, regardless of whether water-drive great enough to be effective is present. This is where the good conservation angle becomes important. Several authorities are quoted to the effect that recovery by a typical water-drive is around 75 per cent as compared with around 40 per cent by complete gas drive. Water-drive is thus nearly twice as effective as gas drive in recovering the original oil, which amounts to saying that gas-expansion drive wastes nearly half of the recoverable oil. The author says that no authority seems to have come forward with a contrary opinion.

It is therefore to be inferred that in the interest of good conservation, production by water-drive should be required wherever this method can be made effective. It cannot be done in every case, but should be done in every case where the proper conditions exist. The advantages are fourfold: (1) a greater amount of oil will be recovered; (2) flowing life of the wells will be prolonged and lifting costs reduced; (3) fewer wells will be required to obtain production; and (4) the bulk of proration can be based on scientific and engineering principles rather than on arbitrary, economic, or political grounds.

The author takes the last proposition as the base for his conclusions. The regulatory bodies should take production under effective water-drive as the engineering and conservation standard (some are now operating under that standard). This standard relieves the authorities of the necessity of determining rates of production by more arbitrary and less scientific methods. There are two disadvantages: a delayed return on investment, and the necessity of grouping small tracts into larger units. Neither of these appears to be insurmountable. Wider spacing allows a greater production per well per day and in the long run is more profitable, and the regulatory body of at least one of the oil-producing states has taken the bull by the horns and is proceeding to merge small tracts into larger ones.

Operation under water-drive where it is present should be obligatory; this would apply to new pools and to old ones except those whose reserves are already nearly exhausted from production under gas expansion. Each case will require competent and impartial engineering consideration.

Correlation of Fuel and Laboratory Research in Secondary Oil Recovery—H. R. Price in OIL AND GAS JOURNAL, Vol. 40 (1941) No. 8, pp. 37-38.

The author lists some fallacies which he finds at the bottom of a number of popular notions regarding the operation of oil reservoirs.

The most popular fallacy included in this list is that producing efficiency can be increased by back-pressure application; although it works in some cases, some pools are irreparably damaged by any method of back-pressuring. These cases can be distinguished in advance by properly designed laboratory procedures.

A generally accepted fallacy of secondary recovery is that most sands are by-passed if there is too much differential pressure from pressure well to producer. While too much pressure sometimes exists, many sands have been irreparably damaged by starting with too low a differential pressure.

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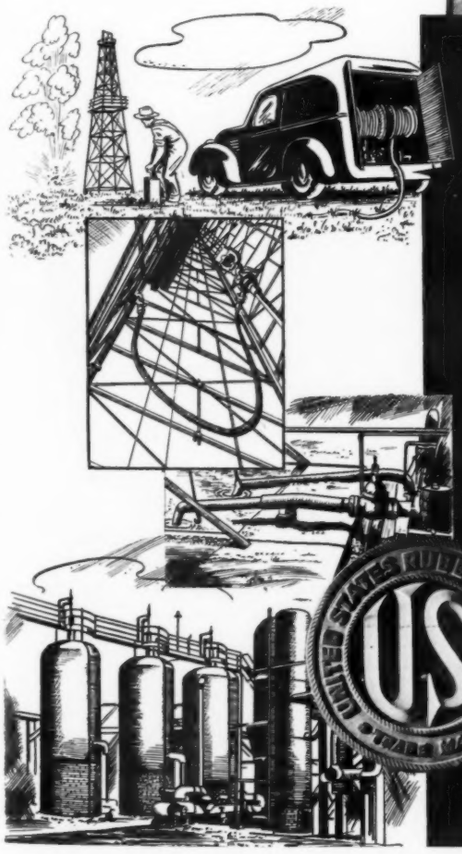

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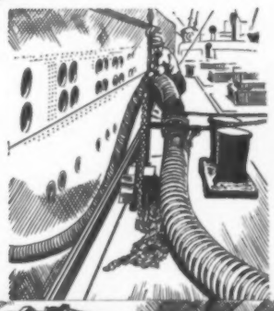

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A third fallacy is that a synthetic representation of a sand body can be reproduced. Too much reliance has been placed on this idea.

By field and laboratory tests, which are listed, practically accurate saturation of oil producing reservoirs can be estimated, but it is a delusion to expect that direct readings of sand saturation can be made from core analysis.

It can be demonstrated conclusively that there is no means of choosing core samples to be tested as representative of the whole section.

By simple demonstration on actual cores it can be shown that the so-called differential shooting in recovery is inefficient and damaging to the ultimate recovery of oil.

After listing these fallacies, the author turns his attention to a proposition which may or may not involve a fallacy. This relates to a method of applying solvents to actual sand bodies in connection with gas-recycling recovery operation, which is said to have been worked out on an economical basis and offers many possibilities. For this process it is claimed that recovery is practically perfect, and that the solvent used can also be recovered by one of several practical methods. It is indicated that the solvent used may consist of light and therefore less viscous petroleum fractions.

Air-drive Experiments as Related to Secondary Recovery—H. Krutter, before 10TH ANNUAL PETROLEUM AND NATURAL GAS CONFERENCE, Penn. State College, May, 1941.

Air drive for recovering oil from old sands has been common in the Venango region since 1932. It is more or less well known to the field operators, but comparatively little laboratory research has been done on its problems. The Pennsylvania Grade Crude Oil Association therefore sponsored a research project on the matter, and the author here makes a report on the progress of the project.

Out of the large number of experiments made on a large number of cores there have come several conclusions that appear to be more or less final. One is that the oil left in the pores of a water-free sand body after no more oil is expelled by means of air is retained to the sharp angles between the sand grains.

The importance of this conclusion will appear from some other facts that were disclosed in the experiments. The author feels that he is fairly safe in saying that a core which is free from water but which has 30 per cent of saturation with oil will not give up any oil when subjected to air drive. This laboratory conclusion is noted to conflict sharply with the fact that in field operations oil may be recovered from properties with only 30 per cent of saturation. The clue to this contradiction is found in the failure of the laboratory to take into consideration the connate water content of the actual oil sand.

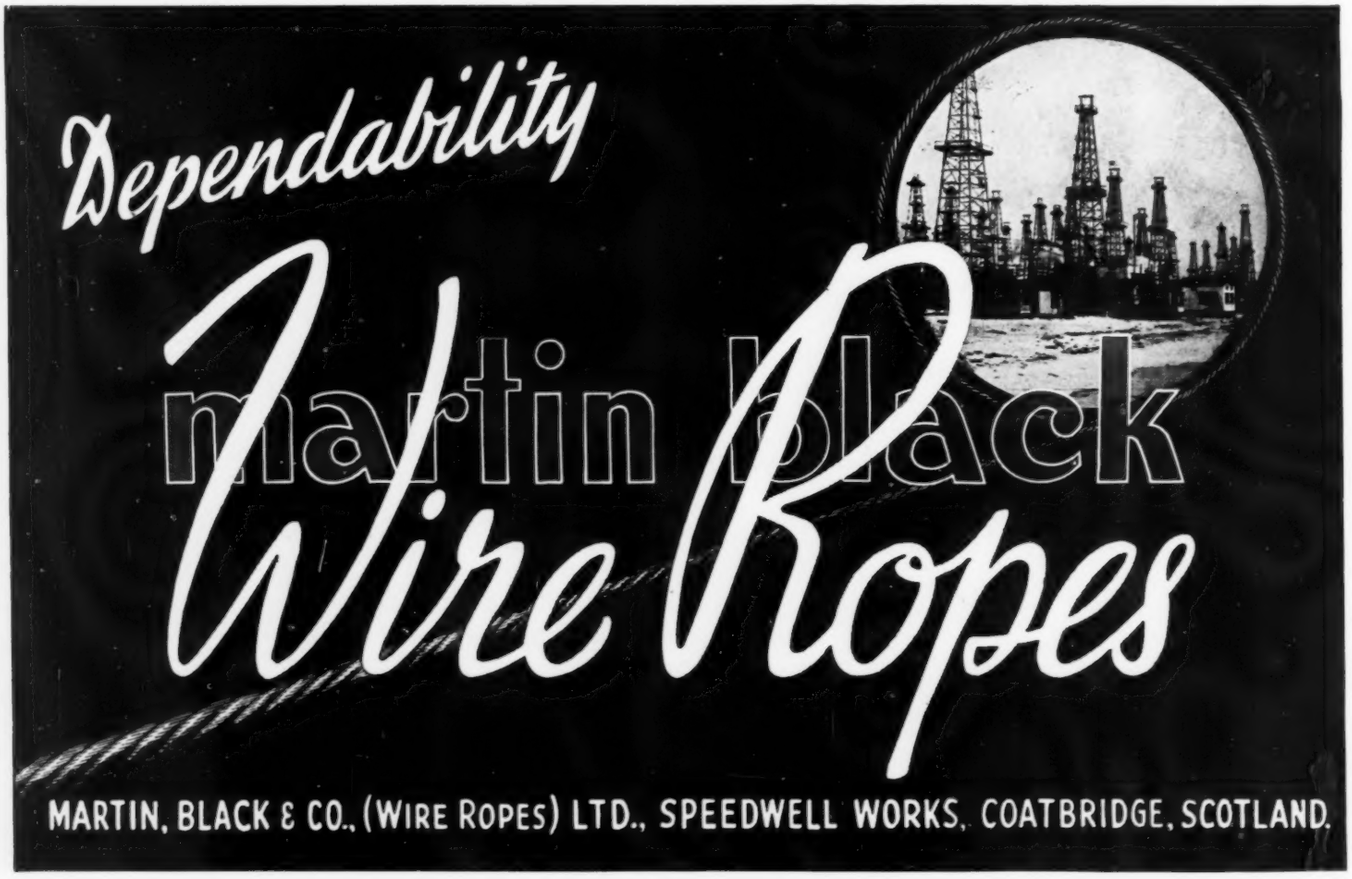
How important this connate water is in the examination of oil sand cores is made to appear from the following considerations. It may be assumed that in many if not most cases oil has migrated into the sand by displacing the salt water originally contained in the sand. In this process the oil would not displace the water from the smaller capillary spaces between the sand grains. The more connate water there is, the more the oil is crowded into the larger pores, from which it is easily expelled by air pressure. Therefore a sand with an oil saturation of 30 per cent may produce oil. The author does not explicitly say so, but it seems to be a fair inference from his work that the percentage of the total oil in a sand that is recoverable by air drive will be the smaller, the less connate water there is to fill the finer capillary spaces. Consequently he strongly recommends that in making a core analysis for recovery estimates, the connate water content should be determined as well as oil saturation.

In one set of experiments cores were used in an effort to obtain light on the much debated question as to whether air pressure in a secondary recovery operation should be low at first and then be increased stepwise to a high value, or whether high air pressure should be applied from the beginning. The experimental data allow the conclusion that it is greatly to be preferred if high pressure is maintained from the beginning.

PIPELINES

Operating Supercharged Diesel Engines in Pipeline Service—J. B. Harshman, before OIL AND GAS POWER DIVISION OF AMERICAN SOCIETY MECHANICAL ENGINEERS, Kansas City, June, 1941.

Diesel engines, like other internal combustion engines, obtain their power by the explosion of a mixture of a hydrocarbon fuel and air in the engine cylinder. The violence and strength of the explosion depends on the quantity of the explosive mixture in proportion to the space in which the explosion occurs. Ordinarily, the internal combustion engine takes in the air at atmospheric pressure. Thirty years ago it was recognized that if a larger amount of air were forced into the cylinder by compression, with more fuel, the explosion would be stronger.



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The above is the principle; the practice has been a long time in developing. It has now reached fair success in Diesel locomotives and some stationary plants, and five years ago Stanolind began experimenting with it for pipe line stations. These experiments have been a mixture of successes and failures. However, sufficient experience has been gained to prove that increasing the horsepower of existing pipeline pumping installations is not only practicable, but economically justifiable. For instance, 250-hp. increase can be obtained by supercharging a 500-hp. engine for an investment of approximately $12,500, including the cost of new gears for increasing the speed of the pump. This is equivalent to $50 per installed horsepower, which is less than half the cost per installed horsepower when purchasing additional pumping units.

The use of supercharging has other advantages which make it attractive for pipeline service. For instance, it frequently becomes necessary to provide a temporary increase in horsepower and pumping capacity at trunk-line stations handling oil from flush fields or for a temporary peak load to certain refineries. After this peak-load requirement no longer exists a large investment is usually left idle or operating at low capacity. If this peak condition is met by supercharging, the turbo-charger and other equipment used in its operation may be moved at a nominal cost to another station, where the additional capacity can be used to advantage.

About the only disadvantage actually encountered in operation of the last two installations has been inability to operate these units at loads below the original rated horsepower of the engine. Although the exhaust-driven turbine is supposed to compensate automatically for load variation, it appears that an excess amount of air is forced into the engine for the quantity of fuel consumed, which results in poor combustion. After operating at reduced loads for a few days it is necessary to remove the turbine rotor and clean out the carbon accumulations.

It is expected, or at least hoped that improvements in design will remove this inconvenience.

Conclusions Based on A. P. I. Coating Tests—Kirk H. Logan, in PETROLEUM ENGINEER, Vol. 12 (1941), No. 6, pp. 100, 102; 104; 106.

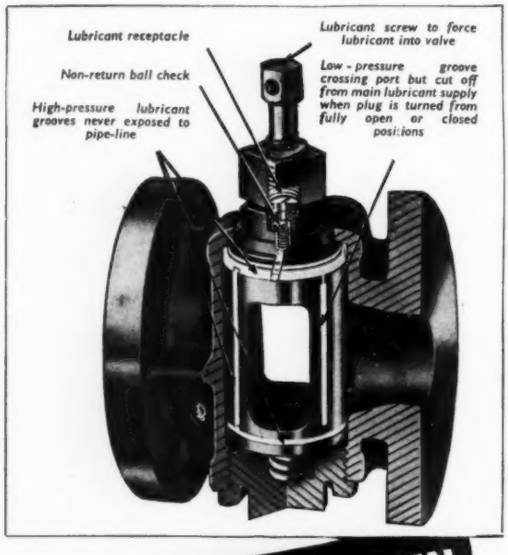
In 1940 the American Petroleum Institute brought to a close an investigation of protective coatings that involved the study of 46 combinations of materials under 15 soil conditions at a cost of more than $100,000. Each of these coatings differed from the others in one to six or more particulars.

The final data indicate that none of the coatings completely protected the pipe at all test sites; only two completely protected the pipe at any test site, and only one afforded complete protection at more than one site. Cut-back coal-tar appears to be the poorest; the best appears to be asphalt mastic, which is rated at 72.5 on a scale of 100; the next best seems to be asbestos-felt reinforced coal-tar enamel, which is rated 30.8. The table of ratings is here reproduced.

Character of Coating	Length examined ft.	Percentage Unaffected	Pitted
Cutback coal-tar	166	1.2	84.5
Coal-tar enamel	152	13.8	62.
Asphalt mastic	213	72.5	2.8
Asbestos-felt shielded coal-tar enamel	202	29.3	27.8
Asbestos-felt reinforced coal-tar enamel	218	30.8	39.9
Asbestos-felt reinforced asphalt enamel	208	20.2	50.5
Cotton-cloth reinforced asphalt	228	0.4	44.1
Steel-shielded, reinforced asphalt	229	5.2	20.1
Cotton-cloth reinforced, chromated, grease	208	0	66

Surveying the whole proposition the author, under whose direction the tests were executed, says that the failure of protective coatings to prevent all corrosin and the occurrence of a serious pit occasionally beneath many of the better coatings have, in the minds of some, over-shadowed the great reduction in corrosion that accompanies the proper use of many coatings. The function of a protective coating is to reduce the annual charges on the pipe line rather than to prevent all corrosion. The best coating is, therefore, the one that will effect the greatest saving, and a coating that prevents all but a few leaks may be a better coating than a more expensive one that prevents all corrosion. As the final report states, the economics of the problem should be considered.

In this consideration some thought might be given to the application of a rather inexpensive coating at the time the line is laid with the expectation of applying additional protection if some part of the line should prove to be inadequately protected. If the original coating has good insulating properties and maintains them, the line may be further protected at critical places by the installation of cathodic protection units. Cathodic protection has a reasonably long and favorable record. At present, data are not available that will enable the engineer to estimate accurately the division of his protection money between coatings and cathodic protection, but there is reason to believe that a proper combination of the two forms of protection will be more economical than either by itself.


Lubricant receptacle
Lubricant screw to force lubricant into valve
Non-return ball check
Low - pressure groove crossing port but cut off from main lubricant supply when plug is turned from fully open or closed positions
High-pressure lubricant grooves never exposed to pipe-line

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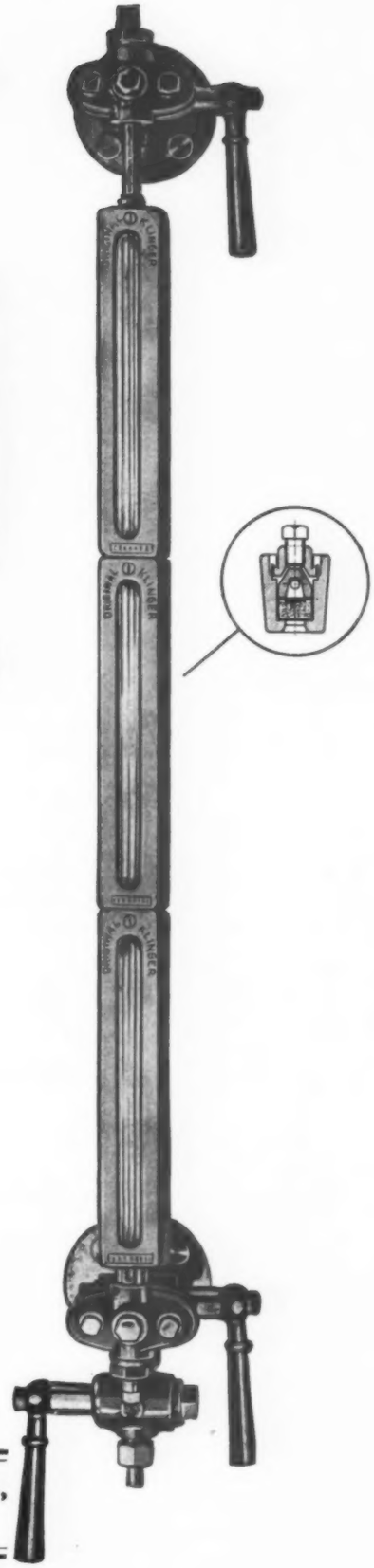

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NATURAL GAS

Use of Natural Gas in Oil Refineries—Frank S. Kelly before American Gas Association, Dallas meeting, May, 1941.

The point of this paper lines in some figures which are intended to impress upon the refiner, particularly the smaller refiner, the value of cracking still gases that are being used as fuel. As a hypothetical case the analysis is given of a typical refinery still gas:

Hydrocarbon	Percentage
Methane	30
Ethane	22
Propane	15
Propylene	13
Butane	10
Butylene	10
Total	100

This typical still gas has a heating value of 1,878 B.t.u. per cu. ft.; and if used as refinery fuel at 10 cents per 1,000,000 B.t.u. it is worth 18.8 cents per 1,000 cu. ft. If this still gas were used in a thermal polymerization plant the byproducts per 1,000 cu. ft. of still gas would be 6.6 gal. of polymer gasoline and 898 cu. ft. of 1,188 B.t.u. fuel gas. The value of the 6.6 gal. of polymer gasoline at the present market price of 5¼ cents per gallon would be 34.6 cents, and the value of the 898 cu. ft. of fuel gas at 10 cents per 1,000,000 B.t.u. would be 10.7 cents per 1,000 cu. ft., or a total value for both products of 45.3 cents. This compares with the 18.8 cents per 1,000 cu. ft. fuel value of the original still gas, or a net difference of 26.5 cents per 1,000 cu. ft. In other words, for every 1,000 cub. ft. of still gas burned as fuel, without processing through a poly plant, the refinery lost 26.5 cents of potential gross revenue.

On this basis a value is figured for the approximately 158,000,000,000 cu. ft. of still gases consumed by refineries in the Mid-Continent, Gulf Coast and California areas. With due allowance for gases already processed through a poly plant this represents potential charging stock for 119,000,000,000 cu. ft. for a poly plant; this stock would produce a potential gross revenue of $31,500,000, which is the difference between the value of the still gas as charging stock for a poly plant versus its value as a fuel gas.

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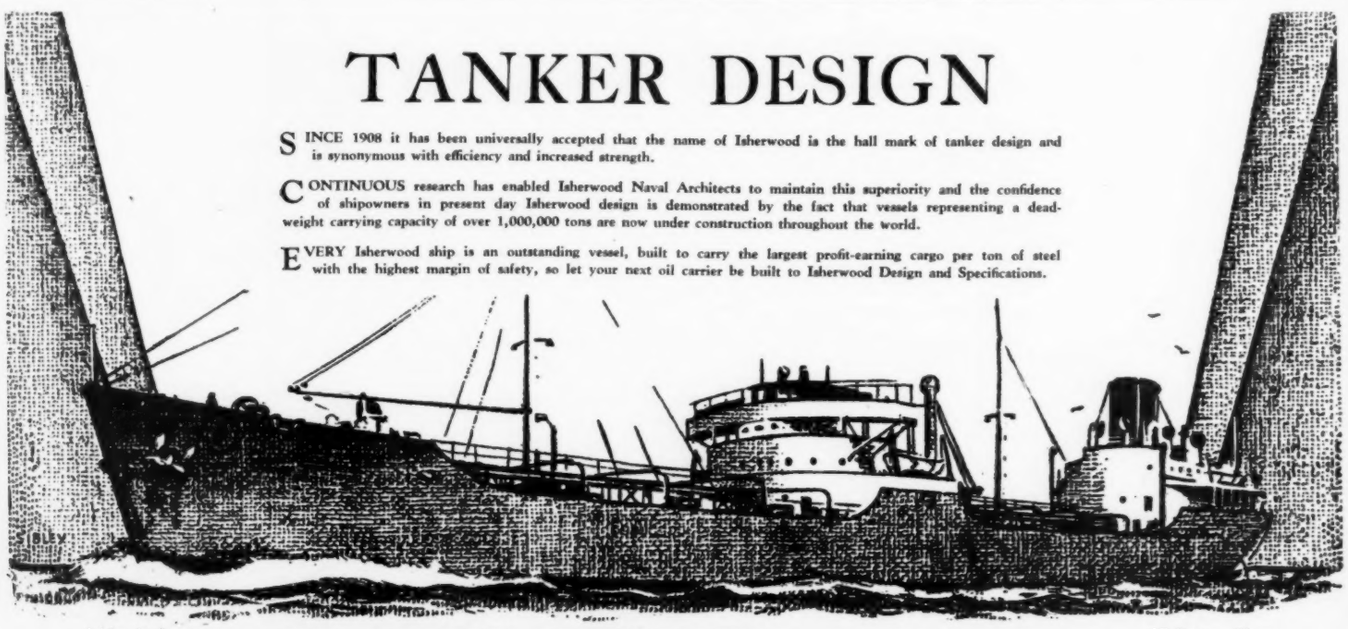

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